Mechanical and physical properties of fibre-cement composites using alternative natural fibres

Kateřina Kochová

Bouwstenen 343

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Mechanical and physical properties of fibre-cement composites using alternative natural fibres

PROEFSCHRIFT

ter verkrijging van de graad van doctor
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door

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Het onderzoek of ontwerp dat in dit thesis wordt beschreven is uitgevoerd in overeenstemming met de TU/e Gedragscode Wetenschapsbeoefening.

Preface

When I started to write this preface, memories came to my mind. It seemed like yesterday when I arrived in the Netherlands and started my long journey. I felt so excited to start another chapter in my life. I knew that it would not be easy, but I like challenges. This incredible PhD journey started on the first of October 2014, and since then, I have studied and performed research in the Building Materials group of prof.dr.ir. H.J.H. Brouwers in Eindhoven University of Technology. During this journey, I realised when you are motivated, you can do anything. Those years gave me knowledge, international travels to conferences, confidence in presenting science, writing articles and meeting international people from all over the world. Therefore, I want to express my gratitude to all these people.

First, I would like to express my great thanks to my promotor, prof.dr.ir. H.J.H. Brouwers, who gave me the opportunity to join the Building Materials group under your supervision, you have given me your supervision, time and energy. I want to express my gratitude to my daily supervisors, dr. ir. Katrin Schollbach and dr.ir. Florent Gauvin supported me in many ways during this amazing and challenging journey. I learned a lot from you, and it was an honour to work with you.

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I want to express my appreciation to all my friends (especially Katarina and Qadeer), which I met in the Netherlands, and we stayed friends until now. Many thanks also go to friends in the Czech Republic who knew me before my PhD journey and told me that I have changed for the better due to this amazing experience. Thank you for supporting me in this journey, and I wish you all the best.

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Kateřina Kochová

October 2022

Mníšek pod Brdy, the Czech Republic

Contents

Chapter 1

1 Introduction

1.1 Materials

Wood-cement composites were developed in the early 20th century and have been used since then as building materials [1]. The main advantage is primarily: resistance to decay and insects, good acoustical and thermal insulating properties, low density (300 to 500 kg/m^3) [1]. The most common use of wood-cement composite, namely wood wool cement board (WWCB), is in parking decks, basement ceilings, floor units, loft conversion, timber frame construction, sound barriers, and acoustic absorption [2].

The main component for making WWCB is wood. Spruce and poplar wood are the most commonly used and are usually obtained from regional forestry. The difference between spruce and poplar wood is: spruce wood is classified as softwood, and poplar wood is classified as hardwood [3]. The second component is a binder, which is generally ordinary Portland cement, but $MgSO_4$ and caustic calcined magnesia (Sorell cement) can also be used. Due to the economic benefits, additives, such as lime, can be used [2].

The use of wood particles in cement has increased rapidly over the past decade, primarily because of improvements in process technology, economic factors and increased concerns about sustainability, renewability and recycling of wood and less consumption of cement [4]. Moreover, large amounts of organic and inorganic waste are generated around the globe from various human activities, such as producing electricity or food (rice husk, wheat straw, bagasse) and the demolition of old structures (buildings, railways) [5,6]. WWCB offers a good opportunity to replace wood and cement with waste products. Cement can be replaced, for example, with fly ash, rice husk ash, and wood can be replaced with natural waste fibres, like coir fibres, rice straw, oil palm fibres or fibres intended directly for processing such as hemp or jute [7]. In this way, new sustainable WWCB can be created with economic benefits by taking advantage of waste products.

Despite the many advantages of natural fibres, there are some issues that need to be considered. Several problems are listed below in this chapter. One of the challenges of natural fibres is their chemical composition. The chemical composition of natural fibres depends on many factors, for example, fibre, location, harvesting, etc. [8], but there are 3 main components: cellulose, hemicellulose and lignin. Cellulose, which is composed of long chains of glucose linked via glycosidic bonds, nevertheless does not have an important effect (absorption effect) on the cement hydration compared to pure sugars due to resistance to degradation [8,9]. On the other hand, hemicellulose is made up of different types, and amounts of monosaccharides, namely arabinose, galactose, glucose, mannose, xylose and sugars acids and can have an effect of cement-fibre composite [10]. Since hemicellulose is degradable these components can be released and influence the hydration of cement paste, which can decrease the curing strength of cement [11]. The third main component in natural fibres is lignin, and it is a high molecular weight randomly linked phenolic polymer [8]. Additionally, natural fibres contain pectin and waxes, where pectin is also located in the fibre cell walls. The function is to provide flexibility and is also a polysaccharide [7,12]. Waxes are a compound of different types of alcohols [7].

1.2 Problem statement

The development of cement-wood composites has been slowed down by a lack of basic understanding of the mechanisms involved in the reaction between cement and natural fibres [13]. Previous researchers have shown that not all wood types and fibres are compatible with cement due to a retardation effect [10,11]. This retardation phenomenon, which varied according to different studies, is not yet fully understood [12–14]. Therefore, several attempts have been made to accurately assess the compatibility of different wood types with ordinary Portland cement (OPC) [19]. However, few researchers are evaluating the compatibility of other natural fibres, particularly waste fibres that can be used for the production of cement-fibre composite. Wood and alternative natural fibres can contain many inhibitory carbohydrates and water-soluble sugars, which may hinder or stop the hydration of cement. However, not all types of sugar have the same inhibitory effect. The quality and quantity of leached carbohydrates and water-soluble sugars depend on the type of fibres and their growing conditions. The effect of these organic retarders has been widely attributed to a mechanism based on the absorption onto the clinker grains and nucleation poisoning of hydrate surfaces and the negative effect of cement hydration [11].

The effect of carbohydrates and water-soluble sugars on cement hydration can be explained by two phenomena. Firstly, carbohydrates can slow down the cement hydration or stop the cement hydration. Calcium-binding capacity is important to consider because general studies about organic retarders have shown that the retarders of cement hydration have a strong chelating group that interacts with calcium which can prevent C-S-H gel formation [19, 20, 22–28]. Many studies have shown that carbohydrates such as sucrose, glucose and fructose have the most significant impact. In 2002, Yasuda et al. [22] have shown that glucose and sucrose are the main cement inhibitors. Later in 2005, Baoguo et al. [23] have added that sucrose has a greater retarding effect than glucose at the same concentration. Juenger and Jennings [25] compared cement with 1wt.% sucrose addition and cement paste without sugar addition using calorimetry measurements. They have found that sucrose causes a retarding effect of cement hydration for several months. The research of Sandermann and Brendel [24] has confirmed that fructose has no particular effect on cement hydration at different concentration levels. Bishop and Barron [20] have presented cement hydration inhibition with sucrose and lignosulfonate (product from the production of wood pulp) in concentrations of 1% and 1.75%. Both materials stopped the cement hydration. However, each material acted through a different reaction mechanism. Sucrose acted through nucleation poisoning/surface adsorption, while lignosulfonates was involved the formation of a semipermeable layer on the cement grains. Sucrose reacted with C_3S but did not react directly with C_3A. Secondly, natural fibres have poor alkaline stability. Carbohydrates and water-soluble sugars have been reported to be hydrolysed in a strongly alkaline environment like cement paste [11]. By-products such as sugar acid-anions or calcium sucrate cation appear to be more effective retarders than the sugars themselves [27]. In 2009, Simatupang [28] characterised the degradation products of glucose and cellulose mixed with cement as dihydroxy-butyric acid, gluco-saccharine acid, gluco-meta saccharine acid, lactic acid and mannose. Organic acids from fibres can suppress cement hydration and attack and destroy the cement bond [29]. Cement-wood/fibre incompatibility can limit the practical applications of fibres in cement-fibre composites.

In general, all of those problems are common to all fibre. The difference is that each fibre has different limitations. For example, sugar cane bagasse has high amount of sugars then coir fibre which has another problem with wax on its surface. Therefore, they need to be treated differently with founding the right solution for them.

1.3 Solutions

Due to the mentioned problems, various attempts have been made to improve the compatibility between cement and wood, natural fibres such as CO_2 injection into the cement matrix, the addition of accelerators or fibre pre-treatments [5,30–32]. The latter is the cheapest and most common way to fix defects of natural fibres by washing the unwanted organic compounds such as sugars, waxes, and oils away after the treatment, thus enhancing cement-fibre compatibility.

Pre-treatment seems to be the most promising method compared to mechanical pre-treatment (e.i. shredding, cutting or milling) [33,34]. However, every pre-treatment has a different optimal condition (temperature, time, concentration). From literature is known that a pre-treatment while using high temperature and concentration for a long time can provide the best results by removing the hemicellulose and soluble sugars. However, these treatments can dramatically damage the main cellulosic structure of fibres, weakening the overall properties of the fibre. Among the most used pre-treatments in the literature, is cold or hot water [35–37]. Moreover, an additive such as $CaCl_2$ can be added to a mixture of cement and natural fibres to accelerate the setting affect hydration process of cement, which has promising results [35,38,39]. On the other hand, nowadays there is a trend towards limiting chlorides in building materials. The most effective, among pre-treatments, are alkaline hydrolyses and acidic solutions (for example HCl). The most common methods of alkaline pre-treatment are NaOH. However, a strong OH- hydrolysis like NaOH can also damage natural fibres [31,40]. A long pre-treatment and applying high chemical concentration can damage natural fibres [41,42]. The optimum conditions also depend on the type of fibres.

1.4 Research aims and strategy

The research is carried out by performing a systematic study to address the above-stated challenges and provide solutions that can be directly applied in the industry. Currently, pre-treatments and natural fibres matrix compatibility are mostly studied for application with polymers not cementitious materials, there are a few research of cement-wood composites. The main work is divided into the following parts:

Part I: Fibres

The objective of the first part of this thesis is, firstly, to characterise natural fibres (bagasse, coir, hemp, oil palm, spruce and water hyacinth). Secondly, to investigate the retardation mechanism of natural fibres on cement hydration, using different types of sugars and fibres themselves.

Part II: Solution – pre-treatment

The objective of the second part of this thesis is to discover the best solution, in combination with effective, environmentally friendly, cheap, etc., for natural fibres (bagasse, coir, oil palm, spruce, and water hyacinth).

Part III: Development of cement-fibre composite

The objective of the third part of this thesis is to evaluate which pre-treatment and fibre is the best option for the development of a new cement-fibre composite using coir and water hyacinth fibres. To create and test properties for a new cement-fibre composite.

1.5 Outline of the thesis

This thesis addresses alternative natural (waste) fibres as a replacement of wood in cement-wood composites and their influence on cement hydration. For many years, in various forms, wood fibres have been mixed with cement to make composite materials such as wood wool cement boards (WWCB) and wood cement-bonded boards (WCBB), collectively referred to as cement wood composites. Recently, the use of natural fibres as a sustainable alternative for reinforcements in cement-based materials has increased significantly. Using natural fibres as a reinforcement in cement-based composites is a challenge due to the microstructure and chemical composition of natural fibres, which can critically affect cement hydration and thus the final composite properties. The research outline of this thesis is presented in Figure 1.1.

Chapter 1 is an introduction to cementitious materials and their problems.

Chapter 2 introduces the literature review of cement-fibre composites with an emphasis on WWCB, their properties and usage. It is followed by introducing new materials (natural waste fibres) as reinforcement in cement-based composite with their advantages and challenges.

Chapter 3 deals with the influence of new natural fibres on the cement hydration reactions. The characterisation of different organic compounds present in fibres is obtained to better understand the problems. Experimental results show that glucose, mannose and xylose in fibre leachates have a significant impact on the cement hydration, slowing the hydration for up to 2 days.

Chapter 4 investigates several pre-treatments to improve the properties of the natural fibres and make them suitable to be used as a reinforcement. An alkaline pre-treatment is used due to many advantages. It does not produce unwanted by-products as acid pre-treatments do and can remove hemicellulose, lignin, wax and oil. Experimental results show that pre-treatment can significantly improve cement-fibre compatibility and modify the surface of the fibres.

Chapter 5 identifies the parameters that influence WWCB quality like mechanical properties, wood microstructure, and cement-fibre compatibility. In this chapter, all three parts of the thesis can be seen. Firstly, the characterisation of fibres and problems had to be found. Secondly, the solution needed to be found; lastly, all of the knowledge from the previous parts had to be put together and applied to create a better product.

Chapter 6 presents coir fibres as the most suitable natural fibre for cement-fibre composite due to their low density, and high thermal conductivity and good cement-fibre compatibility and boards are produced. A comparison between a standard WWCB and a cement-coir composite shows that thermal and mechanical properties are very close.

Chapter 7 describes water hyacinth fibres as a potential material for cementitious building materials. Water hyacinth is a pest and, in several countries, an enormous environmental problem, and there is a question about what to do with those fibres. One of the solutions can be to use it as a reinforcement in lightweight concrete, cement-fibre composite, etc.

Chapter 8 summarises all conclusions of the current thesis and recommendations for present and future research.

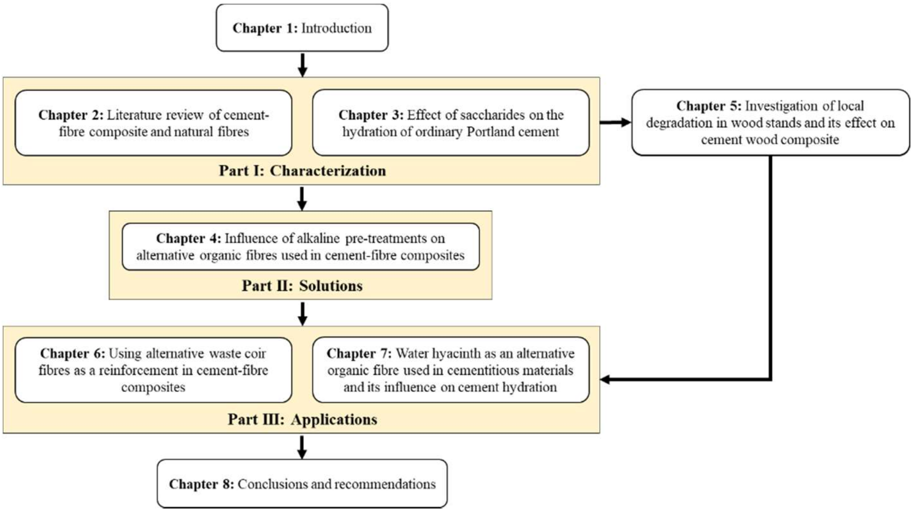


Figure 1.1: Outline of the thesis

Chapter 2

2 Cement-fibre composites and natural fibres

2.1 Definition

Two or more components or phases combined to improve each other's initial properties are called a composite. Two phases are normally incorporated: a matrix and a reinforcement. The reinforcement has functions to provide stiffness and strength of composites [43]. The reinforcement can be ceramic, metal, polymer or natural fibres (cotton, hemp, wood, waste paper or wood or by-product from food crops) [43,44].

A material that involves one or more organic/biological materials is called biocomposite [43,45]. Despite having a mineral matrix, the cement-fibre composite can also be called "eco-friendly" when it contains natural fibres [9].

The matrix works as a transmitter for externally applied loads; consequently, stresses are spread into the reinforcement interface. Another function of the matrix is to protect the fibres from the environment, together with mechanical damage [43]. The matrix can be polymeric or, in this case, cementitious due to usage in the building sector, where it is much more common to use cementitious materials (e.g. mortar, concrete, fibre-cement composite) instead of plastic due to its specific properties (e.g. form a designed shape to hardened element with specific strength and high durability when applied outdoors). Ordinary Portland Cement (OPC) is the most commonly used cement type in building construction. In 2019 it was reported that around 4100 million tons of cement were produced worldwide [46]. Cement provides high mechanical strength as well as longer service life, especially when natural fibres are used. Those properties are due to fibres' mineralisation (or petrification), which is mechanical interlocking between fibre and binder, and mechanical adhesion is achieved [47]. The process of mineralisation is to mix (or soak) fibres with a mineral solution (cement, lime, calcium chloride, etc.) for several minutes when the mineral solution is penetrated into the external layer of fibres [47]. Therefore, the fibres' surface is completely covered, and the composites are protected from the external environment [48].

The main focus of this thesis is to explore the innovative and sustainable way of making bio-based composite for the building sector more especially by working on the reinforcement, namely the natural fibres. In the literature, there are several types of cement-fibre composite. There are three main categories of cement-fibre composite based on their composition: firstly, bio-based lightweight concrete, where natural fibres are used as lightweight aggregate with a diameter of 1-20 mm (Figure 2.1a) [49–51]. Secondly, fibre cement-bonded boards, natural fibres have to be shredded or milled before using mixing with cement and their size is more than 2 mm (Figure

2.1b) [52–54]. Thirdly, wood-wool cement boards, where the size of natural fibres are 250 mm long (Figure 2.2) [4,55,56]. The thesis focuses principally on wood-wool cement composites because they are a perfect candidate to study the development of bio-based composites for the building industry using natural fibres.

a) **b)**

Figure 2.1: Illustration of cement-fibre composite: a) lightweight concrete (wood fibres waste, rice husk ash) [57]**; b) cement-bonded composite (a combination of different chemical additives and press time)** [58]

a) **b)**

Figure 2.2: Illustration of cement-fibre composites – wood-wool cement boards: a) wood-wool cement boards; b) curing process of WWCB [59]

2.2 Wood-wool cement composite

2.2.1 Background

Wood wool cement boards (WWCB) were developed at the beginning of the 20th century and have been used ever since then as building materials [1,4,60]. The advantages of these boards are their good resistance to decay and insects, good acoustic and thermal insulating properties, low density, which is around 300 – 500 kg/m^3, making this product very popular [1,2]. The uses have focused primarily on the advantages of these composites: parking decks, basement ceilings, floor units, loft conversion, timber frame construction, sound barriers, and acoustic absorption [2]. An illustration is presented in Figure 2.2.

The use of wood in cement has increased rapidly over the past decade, primarily because of improvements in process technology, economic factors and increased concerns about sustainability, renewability and recycling of wood and less cement consumption [4]. The most used wood in the production of WWCB in Europe is spruce wood, obtained from regional forestry, and it is classified as softwood [3]. Spruce wood is used due to its availability and lower degradation by the alkaline environment, which is good when cement is used [3,61]. Binder is generally ordinary Portland cement. Magnesium oxychloride cement (Sorell cement) can be used as a binder as well [62]. Due to economic benefits, additives such as lime are added to reduce the price [2].

Moreover, large amounts of organic and inorganic waste are generated around the globe from various human activities, such as producing electricity (e.g. fly ash) or food (rice husk, sugar cane bagasse, wheat straw, etc.) and the demolition of old structures (buildings, railways) [5,6]. WWCB can offer an excellent opportunity to replace part of the whole wood content, and even cement can partly replace waste products. Wood can be replaced with natural waste fibres, like coir fibres, rice straw fibres, oil palm fibres or fibres intended directly for processing such as hemp or jute fibres or waste wood [7,63]. In this way, new sustainable WWCB can be created with economic benefits by taking advantage of waste products.

2.2.2 Production processes

The production process of WWCB is shown in Figure 2.3. Wood wool strands, cement, water and some additives (i.e. dissolved salt) are the most common raw materials used for the production of WWCB. The production process can be divided into several main parts: Preparation of wood, mixing and forming, curing and shipping. Forest trees are harvested, and branches and bark are removed on site. An important part of the WWCB production is to minimise the influence of sugar in the wood, which could influence cement hydration. For that reason, the raw material (wood) is stored in the form of 2 m long logs for 6 - 12 months (depending on the climatic conditions) to leach soluble sugars out. The next step in the process is to cut the wood to pieces in 50 cm than 25 cm. These blocks are shredded on planning machines to get wood wool approximately 1 - 3 mm in width, 0.1 - 0.5 in thickness and 25 cm in length. Before the wood wool fibres are mixed with cement, they are wetted in a salt solution. The water to cement ratio is around 0.5 to 0.8. The wood wool fibres are mixed with cement at a ratio of approximately 0.4 to 0.75 by weight. When the mixing process is done, the mixture of wood wool fibres with cement and water is poured into moulds, and concrete weights are placed on the stacked moulds to compress them. The filled moulds are dried between 12 and 24 hours and demoulded. The finished boards have to pass through a dryer, which removes the moisture from the surface, and the boards are cut to the required format, pigmented (per the customer's specifications) and can be shipped [1,2].

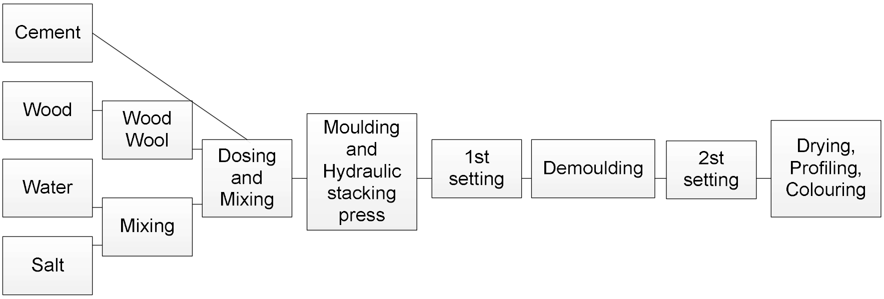


Figure 2.3: Production process of WWCB

In the production of WWCB, several factors can affect the quality of the final product. One of the factors that can be very problematic is a reaction between saccharides in fibres that may hinder or stop the hydration of cement. The amount of saccharides in the wood can vary due to several factors, for example, bark content, geographic location, felling season, tree species and wood storage [11,64]. This phenomenon can cause lower mechanical strength of wood cement composites compared to neat cement. This phenomenon was intensively investigated, but to fully understand cement compatibility with wood and natural fibres, producing wood wool cement boards with new fibre alternatives needs to be studied more [8,9,10]. Therefore, there is a growing number of papers trying to solve these issues. Other factors are geometry and mechanical strength of wood strand, water absorption of wood wool fibres and wood/cement ratio [65]. Many of those factors are typical not only for wood but also for alternative fibres in general.

2.2.3 Improvement of WWCB

When using wood fibres, as well as potential substitutes of wood fibres, natural fibres (NF), several criteria have to be fulfilled in order to make a functional cement-fibre composite. The main criteria for the cement-fibres composite are shown in Figure 2.4. Firstly, a mix design has to be created to achieve the required properties. Secondly, materials need to be chosen, either NF and/or binder. Each NF has a different chemical composition, structure, and, therefore, mechanical properties [33,66]. Thirdly, it is important to find the production process for each fibre and binder. For example, there are two ways of mineralisation: firstly, fibres are wetted, and cement is applied. Secondly, fibres are mixed with the solution of water and cement.

Moreover, the production process for WWCB can also vary in each factory or country. Significant criteria are also the cost of the process. One way to reduce cost is to reuse waste material from production (bad batch, cuts, etc.), which would be discarded. The last and most critical criteria are the final product's properties (acoustic and thermal properties, density, strength, etc.). WWCB has classified based on a standard, and the best way to create a new product is to achieve the same or better properties as WWCB. The standard for WWCB is BS EN 12089, Thermal insulating products for building applications.

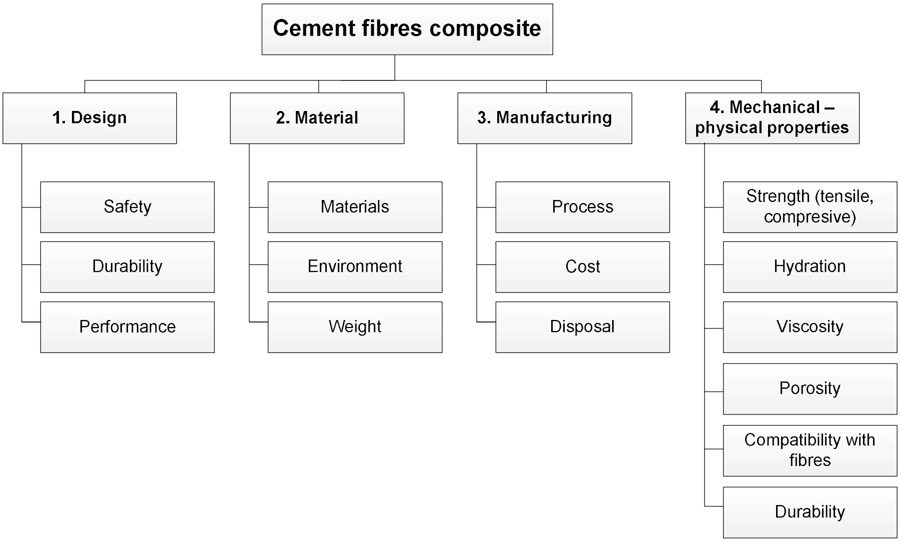


Figure 2.4: Criteria for general cement fibres composite

As mentioned above, an improvement in WWCB can be using NF in many forms (wood, CNF or waste). In general, waste is a huge environmental problem and finding ways to reduce it is a good strategy for the future. Worldwide, lignocellulosic waste can come from three main sources: agricultural by-products, waste from construction and demolition and waste from the wood processing industry [5,7].

In the agricultural industry, a considerable quantity of waste is generated. The waste fibres come from different parts of plants, such as coconut husk, sugarcane bagasse, rice straw and husk, wheat straw and many parts of the oil palm like fibres or shells [5]. For example, the production of cereal straw waste is around 2 billion tons worldwide [67].

Construction and demolition waste can be obtained from buildings, bridges, railways, and fencing poles [5,68]. An example of construction waste is wood from the demolition of old buildings and structures (waste timber). Approximately 20 million m^3 per year of the used timer is produced from demolitions in Japan alone [5]. Due to the fact, that agricultural waste is more available and in huge volumes, this thesis is mainly focused on this waste.

Waste from the wood processing industry is furniture waste generated in many forms as fibre-boards, sawdust, or solid wood pieces. Also, waste is from medium-density fireboards when 22 million m^3 are produced worldwide. There is waste from production and demolition waste after it has been used in the building industry [5]. As it can be seen, the numbers of cellulose waste are high, and usage of this waste can be beneficial for the environment and the construction industry.

2.3 A new type of reinforcement in cement-fibre composites

2.3.1 Natural fibres

Natural fibres (NF) can be divided into two categories: non-renewable (e.g. mineral fibres) and renewable (e.g. plant or animal fibres) [69]. Cellulose natural fibres (CNF) can be subcategorised into bast (e.g. hemp), fruit (e.g. coir), grass/reeds (e.g. corn, bamboo), husk (e.g. barley), leaf (e.g. banana), stalk (e.g. wheat) and wood. Several examples of cellulose/lignocellulose fibres can be seen in Figure 2.5.

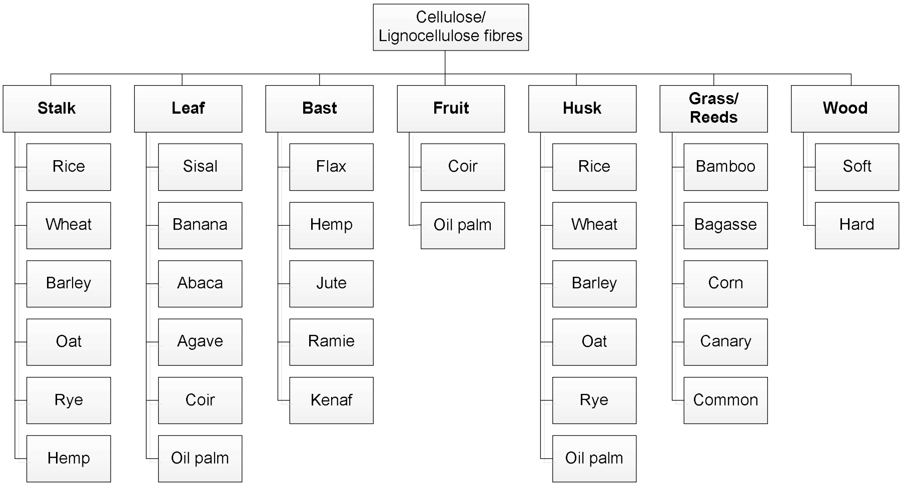


Figure 2.5: Simple classification of cellulose NF

As it was mentioned previously, CNF has many advantages compared to non-renewable (e.g. glass, steel fibres). One of the main advantages of CNF is its low embodied energy. Joshi et al. [70] for example showed that natural fibres are environmentally superior to glass fibres in reinforced composites. In Table 2.1 it can be seen the cumulative energy use selected emissions from ABS copolymer and a hemp-epoxy composite of a side panel for a car using CNF in composite has 45% less energy consumption with lower emissions. On the other hand, phosphate and nitrate's water emissions are higher due to fertilisation during hemp cultivation. Nevertheless, in the hemp-epoxy composite, energy consumption and emissions are from epoxy production. Therefore, when cement is used, there will be a different calculation [70].

Table 2.1: Life cycle environmental impacts from the production of one car side panel [70]

Environmental indicator	Component material	
	ABS copolymer	**Hemp-Epoxy**
Total energy [MJ]	132	73
CO2 emissions [kg]	4.97	4.19
Methane [g]	17.43	16.96
SO2 [g]	17.54	10.7
NOx [g]	14.14	18.64
CO [g]	4.44	2.14
Phosphate emissions to water [g]	0	0.09
Nitrate emissions to water [g]	0.08	12.05

Another example of the sustainability of CNF compared to glass fibre can be observed in Table 2.2, where non-renewable energy is calculated for the production of glass, flax and China reed fibres. The results show that glass fibres have higher pollutant emissions and require 5-10 more energy for production compared to flax and China reed fibres [70].

Table 2.2: Non-renewable energy requirements for the production of different fibres (MJ/kg) [70]

Glass fibre mat		Flax fibre mat		China reed fibre	
Raw materials	1.7	Seed production	0.05	Cultivation	2.5
Mixture	1.0	Fertilizers	1.0	Transport plant	0.4
Transport	1.6	Transport	0.9	Fibre extraction	0.08
Melting	21.5	Cultivation	2.0	Fibre grinding	0.4
Spinning	5.9	Fibber separation	2.7	Transport fibre	0.26
Mat production	23.0	Mat production	2.9		
Total	**54.7**	**Total**	**9.55**	**Total**	**3.64**

Several reasons why to use NF can be concluded. Firstly, NF has a lower environmental impact from production. Secondly, NF composite has higher fibre content, therefore, less pollution from using cement and polymers. Thirdly, fuel efficiency is improved due to the lower weight of composites. Fourthly, the incineration at the end of the natural life of fibres can result in energy and carbon credits [70].

In Figure 2.5, it can be seen that fibers can be made from several parts of a plant; oil palm fibers can be categorized as leaf, fruit or husk (Figure 2.6). Fibres from fruit are similar to coir fibres (long and flexible. Leaf fibres can be used not only in cementitious materials but also as livestock feed. The husk is usually burned and used as a replacement of part of cement, and the trunk of the oil palm tree can also be used as wood fibre [5,71]. Nevertheless, based on the categories, there are also differences in the usage of each material. Not all fibres can be used in the construction industry due to their structure and properties: Indeed, some of the fibres are better suited for the textile or automotive industry (e.g. flax, hemp, jute) due to their unique lightweight structure, processability and sustainability in comparison of plastic fibres [72,73]. Another application for natural fibres is the use of ashes when NF is burned and used as a replacement of cement (e.g. rice and oil palm husk) [74,75]. Hemp, for example, can be used as insulation materials (hemp wool), where cement as a binder is not needed, as well as aggregate in hempcrete, where lime is mostly used [76,77]. There is also a difference in particle size, as was explained above. Small fibres are used for concrete or cement-bonded board, whereas long fibres are used in cement fibre composite.

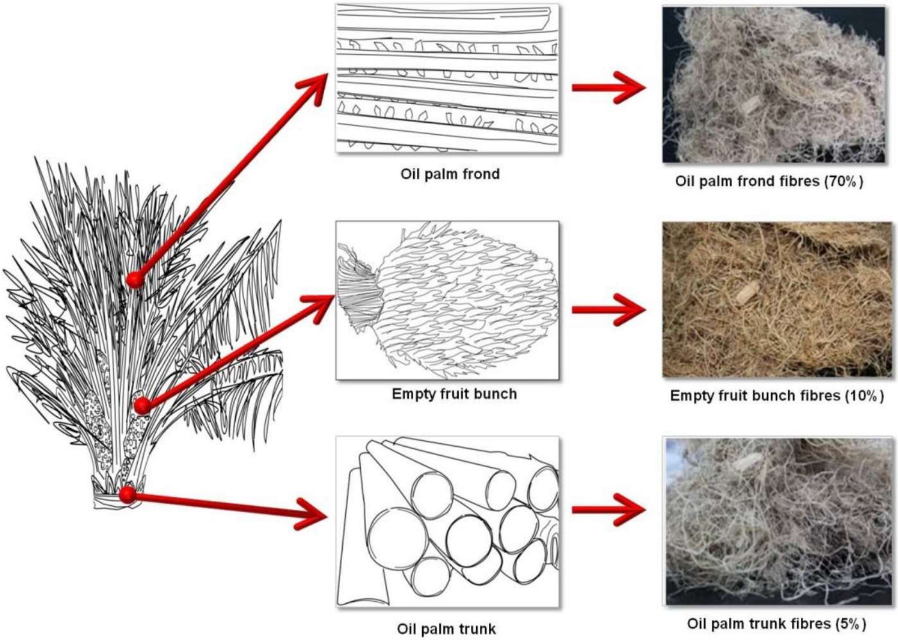


Figure 2.6: Different types of fibres from oil palm tree [71]

As shown in Figure 2.5, there are many fibres that can be used in cementitious materials. However, it is not possible to test all fibres in this study, and a pre-selection has to be made. Each selected fibre has its unique set of properties (mechanical strength, acoustic or thermal insulation, density) and can be a challenge to use in the cementitious matrix due to its chemical composition (e.g. high sugar content), availability (cultivation, pest, waste) and their applications (e.g. fibres in cement board, lightweight aggregate in concrete). The selected fibres used in this study are bagasse, coir, hemp, oil palm, water hyacinth. Spruce is used as a reference, as it has already been used extensively in composites.

This study focuses on sustainability as well as on cement-fibre composites. Therefore, most of the chosen fibres are waste fibres, namely: sugarcane bagasse, coir, hemp or oil palm fibre. Bagasse fibres (Figure 2.7) are obtained from a plant called sugar cane bagasse, which is crushed to extract juice for sugar. Bagasse is available in most countries, making it very inexpensive, and it can be obtained in huge quantities. The length of the fibres may vary, but in general, it is 1-4 mm. Despite its availability, this fibre is challenging due to its very high sugar content [5,78].

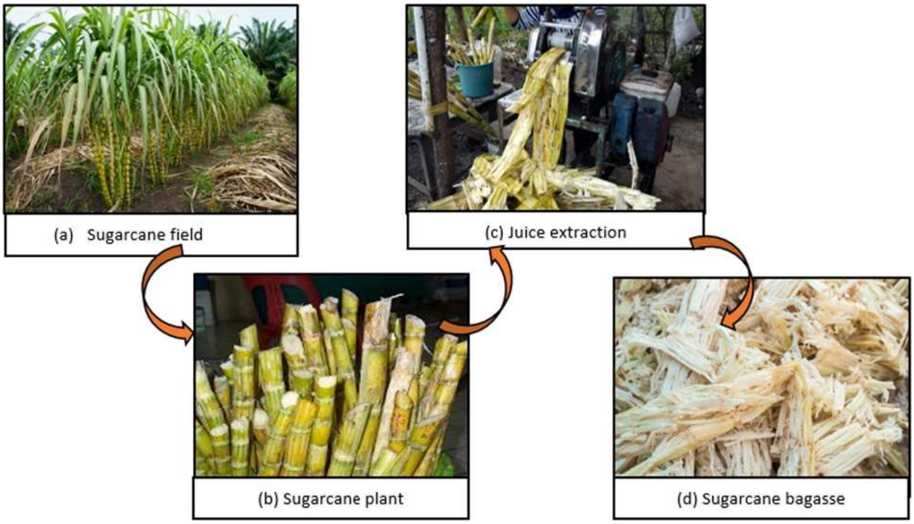


Figure 2.7: Process of sugar cane bagasse [79]

Coir fibres (Fibres 2.8a) are extracted from the husk of the coconut shell after removing copra. Those fibres are strong, flexible and have low thermal conductivity [5,80,81].. In this study, oil palm fibres from empty fruit bunches (Figure 2.6) are used. In general, the oil palm industry is a major industry resulting in 135 million tonnes of waste per year only in Malaysia [79]. The advantage of those fibres is their sustainability due to huge amounts generated during palm oil production. Therefore they are available, and other advantages are good acoustic and thermal properties [5,79]. Water hyacinth (Figure 2.8b) is chosen because water hyacinth is a pest and its environmental problem in China, East Africa and other countries [82–84]. Hence, those fibres are available and inexpensive, and they are lightweight, porous with high absorption levels [85].

a) **b)**

Figure 2.8: a) Cross-section of a coconut [86]; **b) Water hyacinth before and after drying** [87]

Hemp is is not a waste fiber, but can absorb CO_2 during its growth. If it is used to make hempcrete it also captures CO_2 from the air via carbonation, which will be stored into the hemp blocks, making it a carbon-negative material (Figure 2.9) [88]. Another advantage of hemp fibre is its versatility, where every part of the fibre can be used. For example, hemp fibre can be stiff as flax fibre, and shives are porous as water hyacinth or miscanthus.

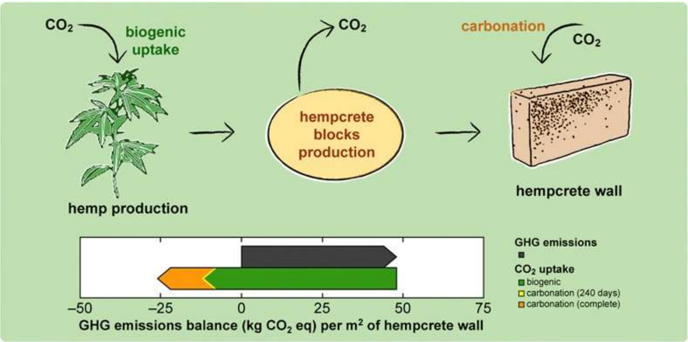


Figure 2.9: Greenhouse gas (GHG) emissions balance [88]

2.3.2 Chemical composition and microstructure of CNF

CNF are natural based materials and the main components of are cellulose, hemicellulose, lignin, pectin and ash. They have similar chemical composition as it can be seen in Table 2.3.

Table 2.3: Chemical composition of fibres [9,71,97–100,89–96], [101]

Fibres	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Bagasse	40 - 62	17 - 35	19 - 25	1.1 - 5
Coir	32 - 52	0.15 - 28	19 - 45	0.9 – 2.8
Hemp	59 - 75	8 - 22	4 - 12	0.5 - 1
Oil palm	41 - 65	22 - 31	19 - 29	2 - 3.2
Rice straw	32 - 57	25 - 33	8 - 25	3.5 – 22.6
Spruce wood	45 - 50	21 - 35	27 - 35	1
Water hyacinth	20 - 53	14 - 35	10	20

Cellulose (Figure 2.10c) is a crystalline polymer composed of a long repeating chain of D-anhydroglucose $(C_6H_{10}O_5)_n$ joined by 1,4-ß-D-glycosidic linkages C1and C4 position in the glucose structure. Nevertheless, it does not have an important effect (absorption effect) on cement hydration compared to the other main components due to resistance to biodegradation [7–9]. Cellulose is known for its resistance to strong alkali, but it is readily hydrolysed to water-soluble sugars by acid [7].

On the other hand, hemicellulose (Figure 2.10b) is different from cellulose in three aspects; firstly, it is a complex amorphous material with lower molecular mass than cellulose and has branched polymers containing five and six carbon sugars (Figure 2.10d), namely arabinose, galactose, glucose, mannose, xylose and 4-O-methyl-D-glucuronic acid [10],102]. Secondly, hemicellulose has chain branches containing pendant side groups, whereas cellulose is a linear polymer. Thirdly, there is a big difference in their degree of polymerisation, with a value for hemicellulose at around 50-300, which is 10 to 100 times less than in cellulose (polymerisation degree at around 10000) [7]. The main problem of hemicellulose is its influence on cement paste hydration, which can decrease the curing strength of cement [11]. Hemicellulose is also very hygroscopic and soluble in alkali, and easily hydrolysed in acids [7].

The third main component in CNF is lignin (Figure 2.10a). It consists of a hydrocarbon polymer with aliphatic and aromatic constituents [7,8]. Lignin is amorphous hydrophobic, and it is insoluble in most solvents [7]. Lignin imparts rigidity to CNF because it is a complex aromatic hydrocarbon polymer. When lignin is not attended to, plants cannot attain high heights [101]. The last components of natural fibre are pectin and wax. Pectin is also located in the cell walls of fibre, and the function is to give flexibility. It is a heteropolysaccharide, and found in bast and fruits [7,12,101]. Wax is a compound of alkaline, fatty acids and different types of alcohols (ketones, aldehydes and other ingredients) [7,101]. There are several factors, which can influence the chemical composition of CNF and therefore change fibre properties. One of the factors is agriculture, such as soil, retting process and weathering. Other factors are climatic and geographical conditions [101].

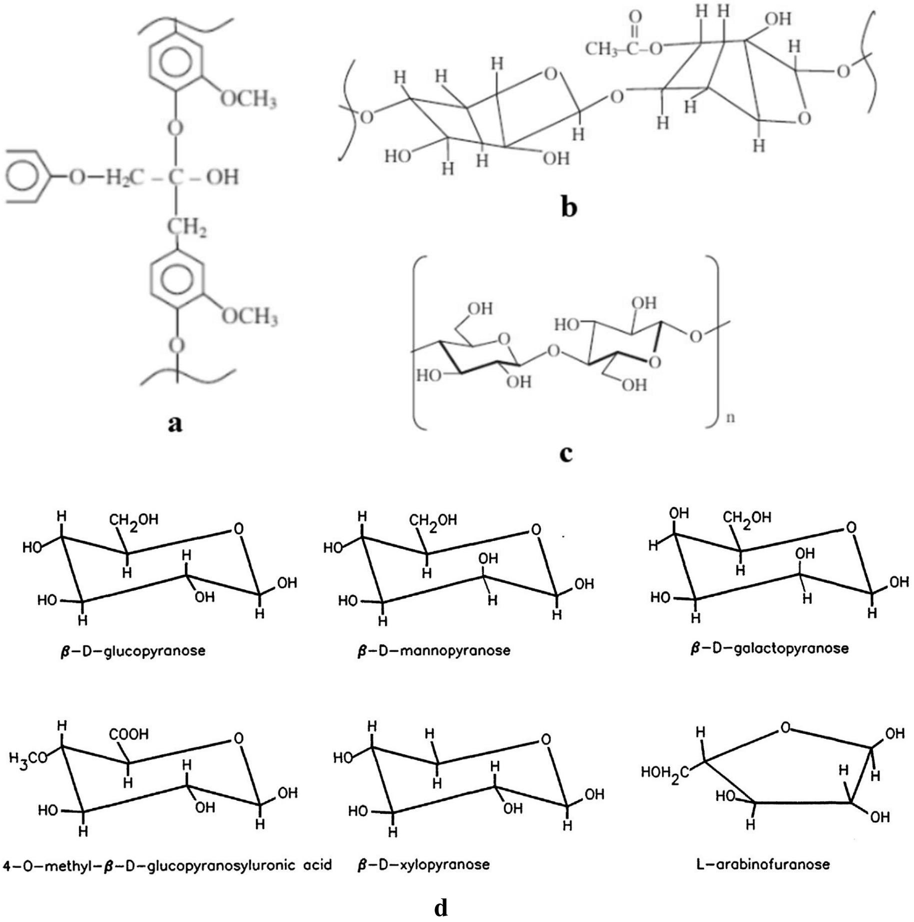
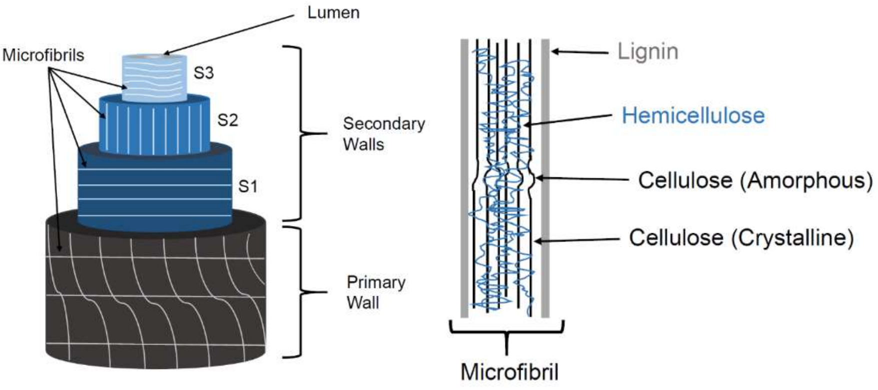


Figure 2.10 Chemical structure: a) lignin; b) hemicellulose; c) cellulose; d) monosaccharides of hemicellulose [102,103]

The structure of CNF (Figure 2.11) consists of hollow cellulose fibrils stuck together by a matrix of hemicellulose and lignin. The structure of each fibre consists of primary and secondary walls, where the primary cell wall is thinner than secondary walls. The secondary wall has three layers, and the thick secondary wall S2 is responsible for the mechanical properties of fibres. The middle layer can be found in a series of helically wound cellular microfibrils formed from long chin cellulose molecules. The microfibrillar angle is the angle between the fibre axis and the microfibrils, where its characteristic value may vary in different fibres. Several parameters are important for the mechanical properties of CNF, namely cell dimensions, defects, chemical composition, microfibril angle and structure of the fibres [7,66,104].



a) **b)**

Figure.2.11: a) Schematic representation of natural fibre; b) Schematic representation of a microfibril

2.3.3 Physical and mechanical properties of CNF

The important mechanical and physical properties of CNF are present in Table 2.4. As mentioned previously, the properties can vary due to several reasons (e.g. chemical composition, microfibrillar angles) [7]. Table 2.3 and Table 2.4 show that when cellulose content increases, tensile strength and young's modulus increase as well and this phenomenon is well known from the literature [7]. As an example of low cellulose fibre (⌀42) is coir fibre, which has lower young's modulus (⌀5) and tensile strength (⌀229) in comparison with high cellulose fibre (⌀67), hemp fibre, where young's modulus (⌀54) and tensile strength (⌀739). Due to the deviation in literature, the numbers of chemical composition and mechanical and physical properties of fibres are listed as an diameter. The microfibrillar angle influences the stiffness of CNF. When microfibrils and fibre axils are parallel oriented, fibres are inflexible and rigid with higher tensile strength [66]. For a comparison between traditional fibres and CNF, glass fibres are added to Table 2.4.

Table 2.4: Mechanical and physical properties of fibres [9,31,98,100,101,105–107,71,72,89–91,93,96,97],[108]

Fibres	Density (g/cm3)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Bagasse	1.25	17 – 27.1	222 - 290	1.1
Coir	1.09 – 1.51	4 - 6	131 - 327	14 - 47
Hemp	1.14 - 1.5	17 - 90	368 - 1110	1.2 – 4.7
Oil palm	0.7 – 1.55	0.6 - 9	100 - 400	2.5 - 25
Softwood	1.5	8.9 - 40	70 - 90	1.5
E-glass	2.5	70	2000 – 3500	2.5
S-glass	2.5	86	4570	2.8

Several criteria have to be evaluated before using these fibres in cement composites. In Figure 2.12, the important criteria for CNF are shown. As mentioned previously, mechanical and physical properties are fundamental and depend on each fibre's chemical composition. The cost goes together with the preparation of fibres. When using natural or even waste natural fibres, the cost can be low, but on the other hand, the preparation and pre-treatment can be expensive.

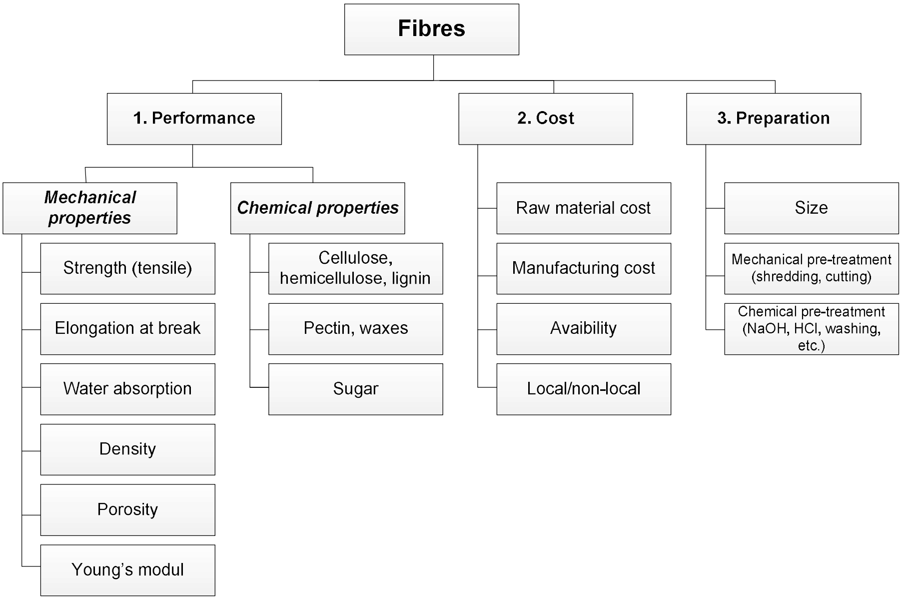


Figure 2.12: Criteria important for CNF to use in cement-fibre composite

2.3.4 Problematic

These advantages that CNF have makes them a good candidate for reinforcement in the cement-fibre composite. However, there are several problems that need to be taken into account when developing new cellulose composites. The problems can be categorised into: the interaction/compatibility between cement and fibres, moisture absorption of fibres, and composite processing. When a new fibre is used, it is possible that a new process or addition step is needed to be added to the process of making cement-fibre composites.

CNF has a hygroscopic behaviour due to the presence of hydroxyl groups in their structure [66]. The result of hygroscopic behaviour and the tubular structure of fibres makes them highly water absorbent [109]. The problems caused by high water absorption can be swelling of the fibres and subsequently formation of voids at the fibre's interface and can lead to low workability of a cement –fibre mix.. They can lead to lower mechanical properties and composite degradation due to destroyed hydrogen bonds between matrix and fibres [110]. In Figure 2.13, micro-cracking of the cement matrix can be observed due to absorbed water and then swelling of fibres.

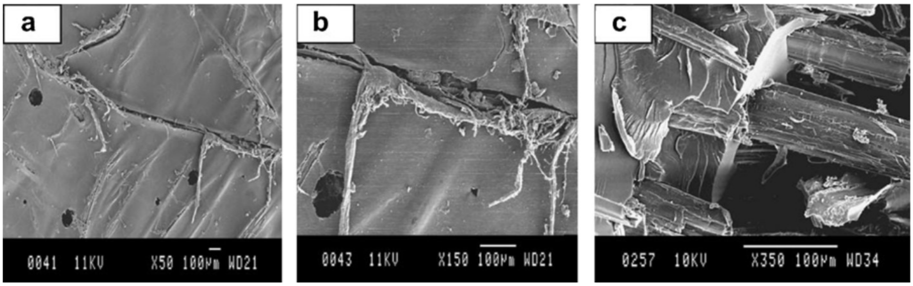


Figure 2.13: Hydrophilic behaviour of natural fibre in cement matrix: a)matrix cracking; b) fracture running along with the interface; c) fibre/matrix debonding due to attack by water molecules [108]

The main problem for the production of cement-fibre composites is often the incompatibility between cement and CNF due to the carbohydrates in the fibres, which may hinder or stop the hydration of cement. The most significant influence can be found from sucrose, glucose, fructose [11]. These components are soluble, especially in an alkali environment and react with the cement paste to slow down cement hydration. It can cause lower mechanical strength of cement-fibre composites compared to neat cement. This phenomenon is caused by nucleation poisoning and sugars forming semipermeable layers on the cement grains. They can also interact with clinkers minerals and accelerate ettringite formation. Another problem caused by sugars is preventing C-S-H gel formation due to strong Ca chelating groups [11,20–27]. In Figure 2.14 is seen the reaction of jute fibre with cement (highly alkaline environment: pH~12) where leached sugar created a protective layer around the partially reacted cement grain. Therefore cement hydration is delayed [111].

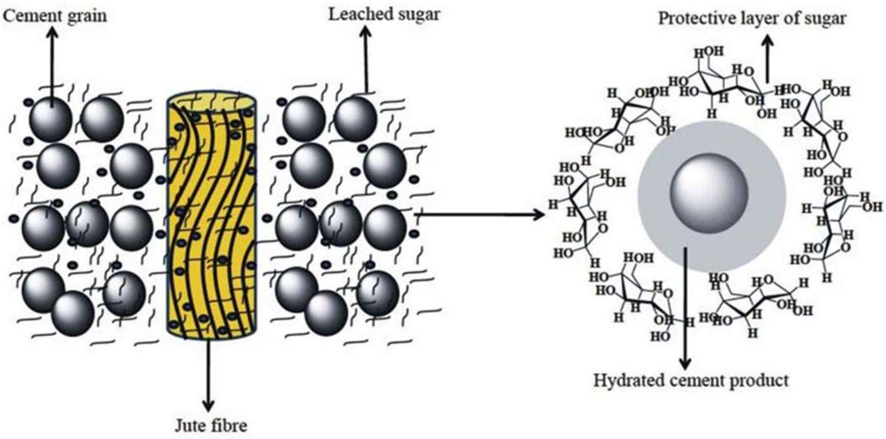


Figure 2.14: A mechanism for the formation of the protective layer of leached sugar (from jute fibre) around the cement grain [111]

Nevertheless, not all types of carbohydrates have the same effect. Glucose and sucrose are observed to have the most significant inhibitory influence due to the promotion of the formation of several adsorbed sucrose layers at hydrating tricalcium silicate surfaces [112]. Sucrose has a more significant retarding effect than glucose at the same concentration because sucrose has a circular structure, which causes a stronger steric hindrance [11]. Figure 2.15 shows an SEM image of hydrated cement samples with additive (sucrose) as a retarder. Regions of broad, flat ettringite rods which grow out of a more amorphous grain coating are observed [20].

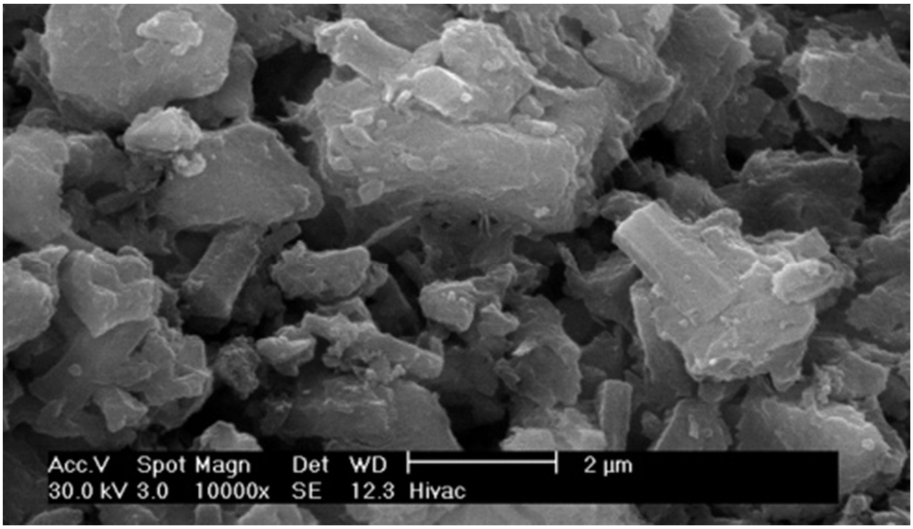


Figure 2.15: SEM image of Portland cement hydrated in the presence of sucrose [20]

One extreme example of sugars in CNF is bagasse fibre. Bagasse is waste from crushed and juiced sugarcane bagasse and contains residues of sugar, and leached carbohydrates (e.g. galactose, glucose) can have retarding effect on cement hydration [113]. The leached carbohydrates' quality and the quantity depend on the type of natural fibres, their growing condition and chemical composition, and the type of wood (hard or softwood). They need to be investigated to fully understand the compatibility of cement with wood and natural fibres to produce wood wool cement boards with new fibres alternatives [11,20,64]. The problems that CNF brings when using them in cementitious materials can have a solution using pre-treatment. This solution can affect not only cement-fibre compatibility by removing unwanted substances but also modifying the surface of fibres and therefore improving the properties of the cement-fibre composite. It can be used for chemical, physical or physicochemical treatments.

2.4 Solutions

The incompatibility between fibres and cement can be reduced or even eliminated by using pre-treatments of CNF. They are three types of pre-treatments: chemical, physical and physicochemical. In general, a pre-treatment is used before mixing fibres with a matrix in composites. Some fibres need only physical pre-treatment, while some need a more severe pre-treatment. Physical pre-treatment is when fibres have to be cut, shred or milled. Chemical pre-treatment is when chemicals are used to remove unsuitable compounds (e.g. sugars) or to modify the fibre's surface. Physico-chemical pre-treatment is a combination of both. Table 2.5 presents different fibres and their possible pre-treatments.

Table 2.5: General review of fibre, their usage and pre-retreatment [5,9,115–124,35,125–129,36,53,67,73,78,113,114]

Fibre	Local in Europe	Size [mm] (harvest/produce)	Mechanical (physical) treatment	Chemical treatment	Product/fibres size [mm]
Bagasse	No	10-40	Shredding/cutting	NaOH, thermal treatment 175-250°C	Cement-fibres composite, particleboard with urea-formaldehyde (chips), particleboard (1-4)
Coir	No	100-300	Shredding/cutting/milling	Cold or hot water, $CaCl_2$, NaOH	Cement-coir board (10-130, 10-60, 10-40), cement-bonded composite (30, 15, 10), particle board-coir, durian peel, urea-formaldehyde (1), binderless board (milling), coir-epoxy composites and coir-PP composites
Corn stalk	Yes	2500-3500	Cutting	Steaming at 170°C	Cement-fibres composite, medium-density fibre-board with urea-formaldehyde (chips)
Hemp	Yes	20, 1200-4500	Cutting	NaOH, EDTA, PEI, $Ca(OH)_2$, $CaCl_2$	Concrete (10, 20, 30mm), Cement-fibres composite (20), polypropylene-fibres composites (10), hemp-PP composite, hemp-epoxy composites
Oil palm	No	10-300	Shredding/cutting	Coldwater, NaOH, latex coating, ɤ radiation, silane, TDIC, acetylation, peroxide, CO_2, accelerator $MgCl_2$	Cement-bonded board (15. 150), fibres-PP composite, oil palm-phenol formaldehyde composite, oil palm-polyester resin composite fibre-PVC composite
Rice straw	No	1000-1800	Cutting/milling	NaOH and HCl, steaming	Binderless board (1. 50), cement-bonded board
Reed	Yes	1000-4000	Cutting	-	Composite with maleic anhydride functionalised polypropylene, virgin propylene, $CaCO_3$, UF-bonded board (3-5.3)
Water hyacinth	No	20-40	Cutting/milling	Hot water, NaOH	Fibre-polyester composites (powder)

Physical pre-treatments can be calendaring, stretching or thermal modification aiming to change the structure and surface of CNF, to improve mechanical bonding between fibre and matrix. Another physical pre-treatment of fibres can be solvent extraction, steam distillation and water pre-treatment [130]. Physico-chemical pre-treatment also includes corona or plasma discharges [130].

Chemical pre-treatment seems to be the most promising method compared to other pre-treatments [33,34]. This type of pre-treatment influences bulk properties by changing the crystallinity structure or/and surface of fibres. Chemical pre-treatments include alkali treatment, acetylation or silane treatment (Table 2.5). Moreover, every pre-treatment has different conditions (temperature, time, concentration). From the literature, it is known that when using high temperature or high concentration for a long time provides better results with removing unwanted substances and modifying fibre's surface. However, these pre-treatments can sometimes damage fibres' main cellulosic structure, weakening the fibre's overall properties making them more brittle. Among the most used pre-treatments in the literature, simple washing with cold or hot water can be used [35–37].

Moreover, the addition of cement curing accelerators such as metal salts ($CaCl_2$, $FeCl_3$ or $Al_2(SO_4)_3$), which can be added to a mixture of cement and natural fibres in order to speed up cement hydration before the inhibitory effect of the leachates, uronic acids, etc. from cellulose fibres can take place [11,35,38,39]. Nevertheless, nowadays, it is a trend to limit chlorides in materials, which are in direct contact with people. It is also problematic in concrete due to its corrosive behaviour to steel rebar. The most effective, between pre-treatment, are alkaline hydrolyses and acidic, using, for example, HCl, which can remove all unwanted soluble compounds but can affect the fibres negatively if not used properly. A long pre-treatment time and applying a high concentration of those mentioned chemicals can damage natural fibres and are not industrially/financially feasible [41,42]. A mechanism for the formation of bonds between hydrated cement products with the cellulose chain of jute fibre is shown in Figure 2.16.

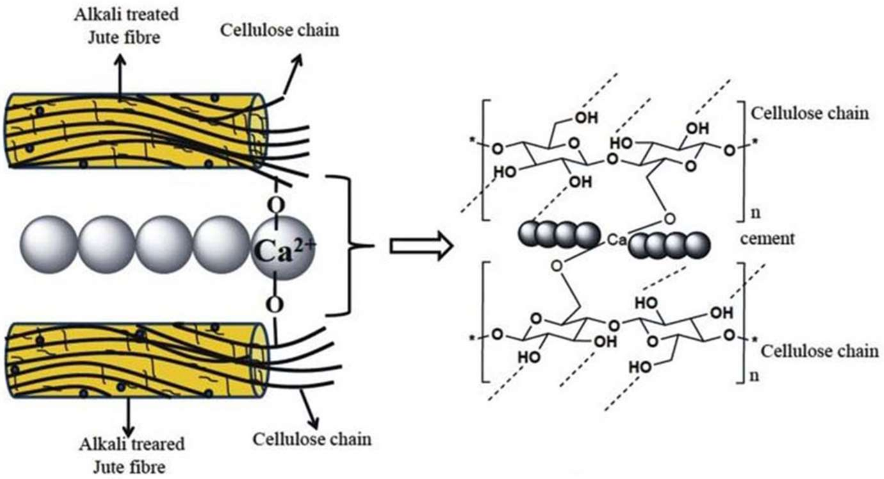


Figure 2.16: A mechanism for the formation of bonds between hydrated cement products with the cellulose chain of jute fibre [111]

Although pre-treatments of CNF have been extensively studied in the past, it appears that alkaline pre-treatments have so far been underused. Nevertheless, alkaline pre-treatments have many advantages. It can break molecules of hemicellulose, increase hydrophilicity and solubility of natural fibres [131]. It can also dissolve lignin by hydrolysing acetic acid esters and decreasing the crystallinity of cellulose [132]. Moreover, alkaline solutions are more sustainable than acids and additives and limit the damage to fibres' microstructure as other pre-treatments, which cause lower strength of the fibre. The most common chemical for alkaline pre-treatment is NaOH. However, a strong OH- hydrolysis like NaOH can damage natural fibres [31,40]. A schema of swelling in CNF can be seen in Figure 2.217. Hydrogen bonds between macromolecules in the CNF ell wall are built by hydroxyl groups in cellulose, hemicellulose and lignin, which is a side effect**.** The main reason for using alkali pre-treatment is to remove lignin, pectin, wax, and natural's oil [133]. The typical surface of CNF before and after alkali pre-treatment is presented in Figure 2.18.

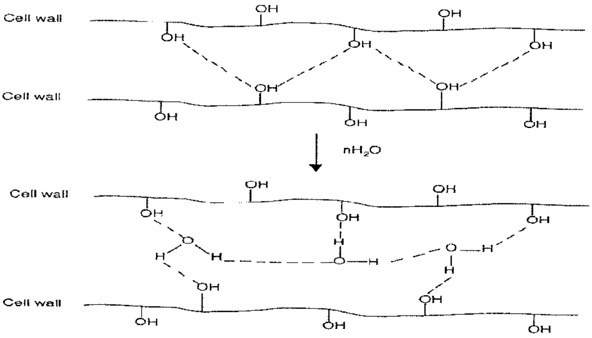


Figure 2.17: Schema of swelling in CNF after alkaline pre-treatment [133]

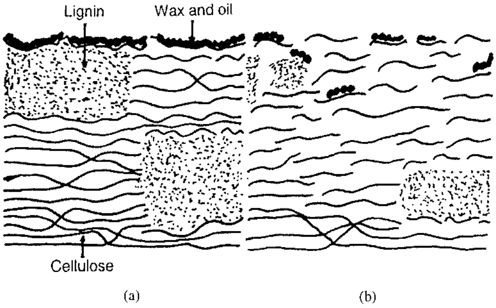


Figure 2.18: Typical structure of CNF: a)Untreated fibre; b) Alkali treated fibre [133]

2.5 Cement-fibre compatibility

A good option to determine if a pre-treatment worked is to assess the cement-fibre compatibility. Compatibility is determined by complex chemical behaviours between cement, fibre and water. [18]. Various attempts have been made to evaluate the compatibility of natural fibres with ordinary Portland cement. The methods that researchers have used include the measurements of hydration characteristics [10,14,27], the improvement and comparison of mechanical properties [135], or the microstructural study of fibre-cement composites [136]. Currently, there is no standard method of measuring the hydration of fibre-cement mixtures. The most commonly used method is the measurement of hydration temperature with adiabatic or isothermal calorimetry due to the relative simplicity of the test, which can help assess the cement-fibre compatibility. The maximum temperature, the time to reach this maximum value, the heat evolved in a specific period of time, and the maximum heat rate of a fibre cement mixture, are the most important calorimetric indicators of cement hydration. This approach is based on measuring the decrease of heat indicators during the hydration process as the organic inhibitor fibres are added into the cement paste. Initially, simple inhibitory indexes between cement and wood were determined and used based on the above-mentioned calorimetric indicators. Still, more complex equations have been developed to reduce inconsistencies in classification [10,14,27,30–34]. An overview can be found in Table 2.6. The first chosen method, presented by Hamchi et al. [18], found a different compatibility evaluation method than previous studies [10,27,30,33]. Therefore, their study determined alternative indicators to overcome inconsistency in the classification presented in previous studies. The alternative indicators are as follow: C_t is the weighted maximum temperature ratio, C_H is the maximum heat ratio and C_A the compatibility factor, the ratio of the amount of heat released from a wood-cement mixture in 3.5 to 24 h interval [18]. The second chosen method is the study of Alberto et al. [140]. In comparison to the study of Hamchi et al. [18], their study determined and classified the wood-cement compatibility by a compatibility factor F_c, which is the ratio of the total energy of the wood-cement hydration reaction Q_c at 48 hours to that of neat cement Q_P. The third chosen method in this study is the cross-compatibility index CX′ developed by Pasca et al. [139]. This new index has taken into consideration most of the exothermic characteristics of the wood-cement hydration behaviour: maximum heat rate, the time needed to reach that maximum and the total heat released within 3.5 to 24 h interval, and it has presented a combination of effects of other indicates. Those are three most commonly used methods to determine cement-fibre compatibility. An overview of the other available cement hydration-based methods for determining the cement compatibility assessments presented by worldwide research is summarised in Table 2.6. There are also presented sample preparation (wood/cement ratio and water/cement ratio).

Table 2.6: Different methods of classification for cement-fibre compatibility

Reference	w/c/w ratio	Base	Equation	Classification Index
Sanderman and Kohler [134]	20:200:100	T_{max}	-	Suitable (T_{max} > 60°C) Intermediately suitable (T_{max} = 50 - 60°C) Unsuitable (T_{max} < 50°C)
Weatherwax and Tarkokw [14]	15:200:90,5	t_{max}	$I = \left(\frac{t_{max} - t'_{max}}{t'_{max}}\right) \cdot 100$	Inhibitory Index (I) Low I value indicates good compatibility
Hofstrand et al. [137]	15:200:90,5	S	$I = \left[\left(\frac{t_{max} - t'_{max}}{t'_{max}}\right) \cdot \left(\frac{T_{max} - T'_{max}}{T'_{max}}\right) \cdot \left(\frac{S - S'}{S'}\right)\right] \cdot 100$	Inhibitory Index (I) Low I value indicates good compatibility
Hachmi et al. [18]	15:200:90,5	T_{max}, t_{max}	$RT = \frac{T_{max}}{t_{max}} \cdot \frac{m_w + m_1}{m_c}$, $CT = \frac{RT}{R'T} \cdot 100$	Weighted Maximum Temperature Ratio (CT) High CT value indicates good compatibility
Hachmi et al. [18]	15:200:90,5	T_{max}, T_r, m_c	$RH = \left(\frac{T_{max} - T_r}{t_{max}}\right) \cdot (m_{cw} + m_{c1} + m_{cc} + m_{cd})$, $CH = \frac{RH}{R'H} \cdot 100$	Maximum Heat Rate Ratio (CH) High CH value indicates good compatibility
Hachmi et al. [18]	15:200:90,5	H	$CA = \left(\frac{A_{wc}}{A_{nc}}\right) \cdot 100$	Area Ratio (CA) Compatible (CA > 68%) Moderately compatible (28% < CA < 68%) Not compatible (CA < 28%)
Wei at al. [64]	15:200:90	T_{max}, t_{max}	-	Least (T_{max} > 50°C and t_{max} < 10 h) Intermediate (T_{max} > 40°C and t_{max} < 15 h) Highly (T_{max} < 40°C or t_{max} > 15 h)
Alberto et al. [140]	80:200:200	Q	$F_c = \left(\frac{Q_c}{Q_p}\right) \cdot 100$	Compatibility Factor (FC) High FC value indicates good compatibility
Okino et al. [138]	-	t_{max}	$I = \left(\frac{t_{max} / t'_{max}}{t'_{max}}\right) \cdot 100$	Low inhibition (I < 10) Moderate inhibition (I = 10 - 50) High inhibition (I = 50 - 100) Extreme inhibition (I > 100)
Pasca et al. [139]	-	T_{max}, H_{rmax}, H	$CX' = \sqrt[3]{\left(\frac{HR_{max} \cdot HR_{3.5} - 24 \cdot t'_{max}}{HR'_{max} \cdot HR'_{3.5} - t_{max}}\right)} \cdot 100$	Compatibility (CX') High CX' value indicates good compatibility

w/c/w ratio – wood/cement/water ratio, apostrophe (′) – represents neat cement, T_{max} – maximum temperature, t_{max} - time to reach T_{max}, S – slope of the time temperature curve, H – hydration rate, Q – total heat evolution, I, C_T, C_H, C_A, F_c, CX′ - compatibility factors, m_w – mass of water,
m_l – mass of wood, m_c – mass of cement, T_r – room temperature, mc_w – thermal capacity of water, mc_l – thermal capacity of wood,
mc_c – thermal capacity of cement, mc_d – Dewar flask, A_{wc} – area under the hydration heating rate curve from 3.5 – 24 h of wood cement mixture, A_{nc} – area under the hydration heating rate curve from 3.5 – 24 h of neat cement mixture, Q_c – total heat evolution at 48 h of wood cement mixture, Q_p – total heat evolution at 48 h of neat cement mixture, H_{Rmax} – maximum heat rate of wood cement mixture , H'_{Rmax} – maximum heat rate of neat cement mixture, $H_{3.5-24}$ – total heat released by wood cement mixture in 3.5 – 24 h interval, $H'_{3.5-24}$ – total heat rate released by neat cement mixture in 3.5 – 24 h interval

2.6 Conclusion

In this chapter, the literature review was introduced in this study. The fibres, their characteristics, problems, and solution can be summarised:

- Large amounts of organic and inorganic waste are generated worldwide from various human activities, such as producing electricity, food and demolishing old structures. In the agricultural industry, a considerable quantity of waste is generated. The waste can be composed of different parts of the plant, such as coconut husk, sugarcane bagasse, rice straw and husk, wheat straw and many parts of the oil palm like fibres or shells.
- Fibre-cement composites can offer an excellent opportunity to replace wood completely from WWCB by using other cellulose fibres. In this way, new sustainable fibre-cement composites can be created with several economic benefits and take advantage of waste products' usage.
- Pre-selection of fibres is based on their chemical composition, mechanical and physical properties, and they have to be environmentally friendly. The selected fibres used in this study are bagasse, coir, hemp, oil palm, water hyacinth and spruce, which is used as a reference.
- Several problems have to be addressed in this study. The hygroscopic behaviour of CNF can result in swelling in fibres and subsequently form voids at the fibre's interface, leading to low mechanical properties and composite degradation due to destroyed hydrogen bonds between matrix and fibres and can lead to low workability of a cement –fibre mix. Another problem is the incompatibility between cement and CNF due to the fibres' carbohydrates, which may hinder or stop cement's hydration.
- The incompatibility between fibres and cement can be reduced or even eliminated by using pre-treatment. The most commonly used pre-treatment is alkaline pre-treatment, which can remove lignin, pectin, wax, and natural oils.

Chapter 3

3 Effect of saccharides on the hydration of ordinary Portland cement

K. Kochova, K. Schollbach, F. Gauvin, and H.J.H. Brouwers, "Effect of saccharides on the hydration of ordinary Portland cement," Constr. Build. Mater., vol. 150, pp. 268–275, 2017

3.1 Introduction

For many years, in various forms, wood fibres have been mixed with cement to make cement-wood composite materials such as WWCB or WCBB. The use of a cellulosic material as filler or reinforcement in these composite materials has significantly increased over the past decade thanks to important improvements in process technology, better economic incentives and increased sustainability concerns such as renewability and recycling of wood materials [4–8]. Nowadays, a large amount of inorganic and organic waste is generated with a substantial environmental impact (waste dumps, pollution, etc.) [9,10]. These waste resources can be used to develop sustainable construction materials, for instance, cement-fibre composites [7].

However, the development of cement wood composites has been slowed down by a lack of understanding of the mechanism involved in the reaction between cement and natural fibres [13]. Previous researchers have shown that not all wood types are compatible with cement. Generally, there is a retardation of cement hydration, lowering the strength of the composite material below the requirements or even causing the disintegration of WWCB boards after compression [13–15]. The cause is saccharides contained in wood and alternative fibres. [11]. Natural fibres contain different saccharides with different water solubility due to the different structures of the saccharides and the fibres themselves. Those that can be dissolved create leachates that can be analysed, explaining how much and which saccharides, particularly monomeric sugars, are leaching from the fibres and how they could impact the cement-fibre composite. The quantity and type of leached saccharides depend on the type of fibres and their growing conditions. However, not all types of sugar have the same inhibitory effect. In 2014, Na et al. [11] reported that glucose and sucrose have a greater retarding effect than others sugars.

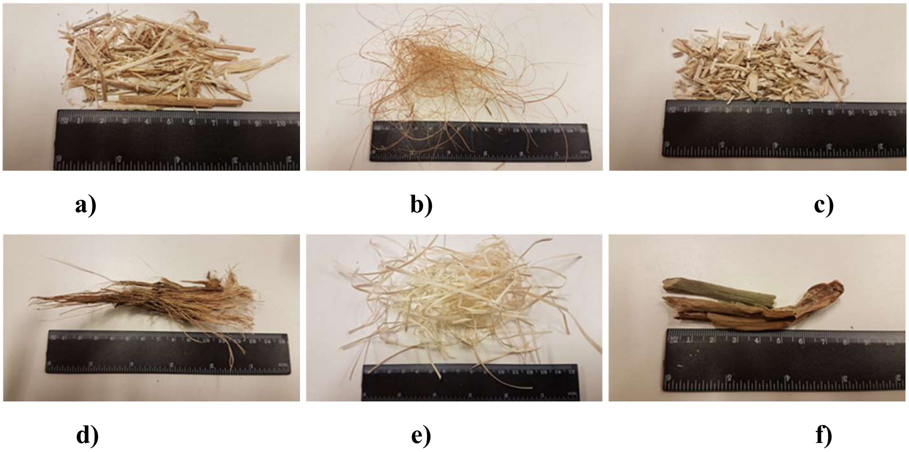
The effect of saccharides on cement hydration can be explained by different phenomena. Firstly, the calcium-binding capacity is important to consider because general studies about organic retarders have shown that they have strong Ca$^-$ chelating groups, which can prevent C-S-H gel formation [16–24]. Another effect is that sugars act through nucleation poisoning/surface adsorption forming semipermeable layers on the cement grains. They can also interact with different clinker minerals differently. For example, sucrose reacts with C3S but does not react directly with C3A and accelerate ettringite formation, which it shows at early stages [20]. Another aspect to consider is the instability of some saccharides in a highly alkaline environment, such as cement paste (pH~13). The degradation products were more efficient than the original wood extractives at inhibiting cement hydration [11]. By-products such as sugar-acid anions or calcium sucrate cations appear to be more effective retarders than the sugars themselves [21]. In 2009, Simatupang [28] characterised other degradation products of saccharides mixed with cement as dihydroxy-butyric acid, gluco-saccharine acid, gluco-meta saccharine acid, lactic acid and mannose. Organic acids, like uronic acids, can suppress cement hydration and damage cement hydration products [26,27]. Several studies have investigated the effect of sucrose and glucose on cement hydration by using calorimetry, showing that sucrose had a strong retarding effect on cement hydration for up to several months [19,20,22].

These investigations show that the hydration of cement in the presence of fibres is far more complex than the sum of hydration reactions of the individual minerals with saccharides. This study focuses on the influence of different little investigated natural fibres on cement hydration. Using leachates is a novel way to investigate this interaction. The fibres studied are bagasse, coir husk fibres (coir), hemp, empty fruit bunches from oil palm trees, water hyacinth, and spruce wood. Spruce wood is taken as a reference since it is commonly used for the production of cement fibres composites and is known to have relatively little influence on cement hydration [4]. The impact of saccharides on OPC hydration is investigated by adding pure fructose, glucose, sucrose, lignin or cellulose to cement pastes. Chemical characterisation of the leachates is performed in order to explain the interaction between OPC and fibres. The most problematic leached organics are monomeric sugars and acids – arabinose, galactose, glucose, mannose, xylose, galacturonic and glucuronic acids [29–32]. The monomeric sugars and the organic acids, including acetic acids concentration, are characterised by high-performance anion-exchange chromatography (HPAEC). The concentration of uronic acids is measured by gas chromatography (GC). The chemical composition of natural fibres is determined by HPAEC following the Tappi standards. Cement hydration was studied by calorimetry to determine the most dominant factor affecting the hydration of cement. The aim is to compare saccharides with leachates of fibres and explain the differences between different saccharides and leachates on cement hydration.

3.2 Materials and methods

3.2.1 Materials

Fructose (purity of 99.0%), glucose (purity of 99.5%), sucrose (purity of 99.5%), lignin were provided by Sigma-Aldrich, and microcrystalline cellulose (20-160 μm particle size) was produced by Merck KGaA, Germany. Six types of natural fibres were studied (Figure 3.1). Bagasse, coir, hemp, oil palm – empty fruit bunch and water hyacinth were provided by Wageningen Food & Biobased Research, the Netherlands, and spruce wood was provided by Knauf Insulation, the Netherlands. Their general chemical composition measured in this study, and comparison values from the literature, are shown in Table 3.1. The chemical composition of natural fibres was determined by Tappi T222, Tappi UM250, Tappi T264 and HPAEC. Measurements were done two times. Spruce wood and natural fibres samples were stored in plastic bags at room temperature until use. CEM I 52.5R (OPC) from ENCI, the Netherlands, was used in this study as a binder. The chemical composition of the OPC is given in Table 3.2.


a) **b)** **c)**

d) **e)** **f)**

Figure 3.1: Natural natural fibres: a) Bagasse; b) Coir; c) Hemp; d) Oil palm; e) Spruce; f) Water hyacinth

Table 3.1: Chemical composition of natural fibres used in this study and presented in the literature [38–51]

Fibres		**Cellulose [%]**	**Hemicellulose [%]**	**Lignin [%]**	**Ash [%]**	**Extractive [%]**
Bagasse	*Literature*	30.0 – 55.2	16.8	19.8 – 25.3	1.1 – 5.0	13.8
	Analysis	**34.2**±0.9	**40.1**±0.8	**11.9**±0.3	**3.9**±0.03	**18.6**±0.15
Coir	*Literature*	32.0 – 43.4	0.2 – 31.1	20.5 – 45.8	2.2 – 4.8	4.2
	Analysis	**36.6**±0.15	**37.0**±0.15	**22.2**±0.05	**1.9**±0.04	**5.7**±0.05
Hemp	*Literature*	55.0 – 68.0	10.9 – 16.0	4.0 – 10.0	-	3.9
	Analysis	**37.4**±1.9	**41.5**±1.8	**17.2**±0.2	**2.5**±0.12	**4.9**±0.05
Oil palm	*Literature*	29.0 – 65.0	12.0 – 38.0	13.0 – 37.0	1.0 – 6.0	8.6
	Analysis	**32.8**±1.93	**42.7**±1.99	**14.9**±0.21	**7.8**±0.02	**11.3**±0.1
Spruce wood	*Literature*	47.0	25.3	27.7	-	1.7
	Analysis	**41.6**±1.08	**37.3**±1.1	**19.4**±0.01	**0.4**±0.02	**2.2**±0.02
Water hyacinth	*Literature*	20 – 53	14 – 35	10	20	17.8
	Analysis	**37.9**±3.62	**37.6**±3.62	**6.6**±0.04	**16.8**±0.17	**23.6**±0.21

Table 3.2: Chemical composition of ordinary Portland cement CEM I 52.5R used in this study

Chemical composition	[%]
CaO	64.60
SiO_2	20.08
Al_2O_3	4.98
Fe_2O_3	3.24
K_2O	0.53
Na_2O	0.27
SO_3	3.13
MgO	1.98
TiO_2	0.30
Mn_2O_4	0.10
P_2O_5	0.74
Cl^-	0.05

3.2.2 Methods

3.2.2.1 Leachate preparation

Fibres were dried at 60°C to constant mass and soaked for 2 hours at 80°C in distilled water (water/fibres ratio of 5:1). Filtrate and fibres were separated with filter paper. The pH of the fibre leachates was determined by a pH Meter (Metrohm 780) after the leachates were cooled down to room temperature. Then, cement was mixed with the fibre leachate instead of water. The leachates were compared with cement mixtures with additionally added saccharides. Plain OPC mixed with water is used as a reference.

3.2.2.2 Calorimetry measurements

Calorimetry was performed with a TAM Air Isothermal calorimeter at a constant temperature of 20°C. All sugars, lignin, cellulose and fibre leachates were mixed with OPC and water. The percentage of sugars and lignin mixed with OPC were chosen as follows: 1.0, 0.5 and 0.2 wt%, the amount of cellulose was 1.0 wt% (all based on cement). For glucose, weight fractions of 0.1, 0.05, 0.02 and 0.01 wt% were also measured. The water/cement ratio was kept constant for all prepared mixes (w/c = 0.5). After mixing, the samples were placed in the calorimeter to observe and determine the cement hydration behaviour. The measurements were done three times. The standard deviation of calorimetry results is about 5%.

3.2.2.3 Concentration of monomeric sugars

The monomeric sugars concentration in the different leachate solutions was determined by high-performance anion-exchange chromatography (HPAEC) after H_2SO_4 hydrolysis. The solution is freeze-dried (1 – 4 ml of leachates) and vigorously mixed in Pyrex test tubes with 150 µl of ice-cold H_2SO_4 (12 mol.L^{-1}) in a water bath at 30°C for one hour. Samples were then removed from the water bath and mixed with an H_2SO_4 (4%) solution. Samples are then placed in an autoclave for 60 min at 120°C. After being cooled down, 5 mg of ribose was added to each sample as an internal standard. Hydrolysed leachates were diluted with deionised water at a different ratio (from 1:10 to 1:100) prior to analysis. Measurements were done with a Thermo Scientific Dionex ICS-5000 system. Samples were separated on a Dionex CarboPac PA1 carbohydrate column.

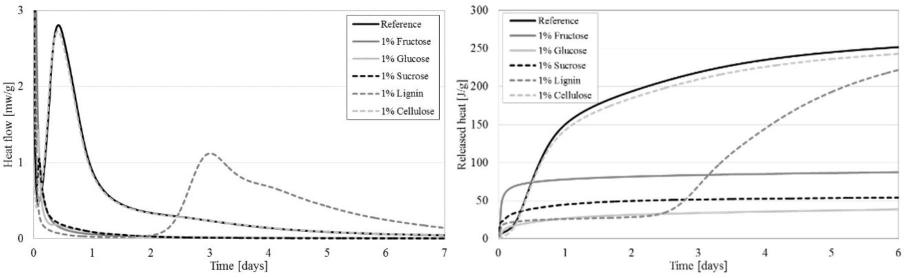
3.2.2.4 Concentration of uronic acid

According to Sundberg, the concentration of uronic acids was measured by gas chromatography (GC) after methanolysis [151]. Samples were lyophilised and then hydrolysed in 2 M methanolic HCl at 100°C for 5 hours, followed by the addition of pyridine and sorbitol as an internal standard at room temperature. After evaporation under N2, samples were silylated overnight with HMDS (hexamethyldisilazane, Sigma-Aldrich) and TMCS (trimethylchlorosilane, Sigma-Aldrich) in pyridine, injected into a GC/FID system (7890A, Agilent Technologies) at 260°C, and separated on an HP-5 column (30 m, 0.32 mm ID, 0.25 µm film thickness) using the following temperature program: 150°C for 1 min, 150°C to 220°C at 4°C/min, 220°C to 320°C at 20°C/min, 320°C for 6.5 min. Calibration was done using identically treated authentic standards of D-glucuronic and D(+)-galacturonic acids.

3.3 Results and discussions

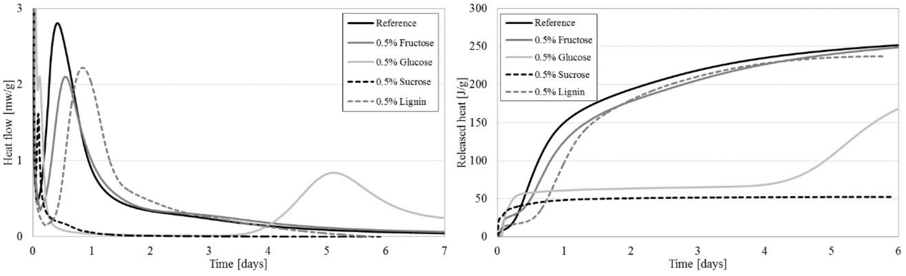
3.3.1 Effect of saccharides on the hydration of cement

Figure 3.2-3.4 depicts the calorimetry measurements of the effect of pure saccharides and lignin on cement hydration. Figures 2a-4a show the heat flow during the exothermic reaction of OPC over time. Figures 3.2b-3.4b show the total cumulatively released heat during that reaction. The heat flow shows the kinetics of the hydration, indicating retardation in reactions. The total cumulative heat gives an estimate of how far the system has hydrated. For the released heat of the different cement pastes, there is a general trend that the initial heat within the first hours of hydration was higher with saccharides and lignin compared to the reference. A possible reason for that could be an increased initial dissolution of phases, including sulphate phase promoting the initial formation of ettringite. The higher the concentration of sugars, the later the maximum heat flow of the main hydration occurs due to cement retardation. It can be explained because sugar decreases the concentration of Ca^{2+} ions in the cement pore solution and delays the formation of hydration products. Figure 2a shows that the addition of 1% cellulose to the cement paste cured at 20°C does not have a retarding effect, but it causes the slight acceleration of cement hydration. A likely reason for this is that it provides additional crystallisation seeds for the hydration products, which can slightly speed up the reaction [152]. The released heat after 24 hours (Figure 3.2b) is almost the same as for the reference. Since cellulose does not interact with cement to cause retardation, no further characterisation with cellulose was done in this study.



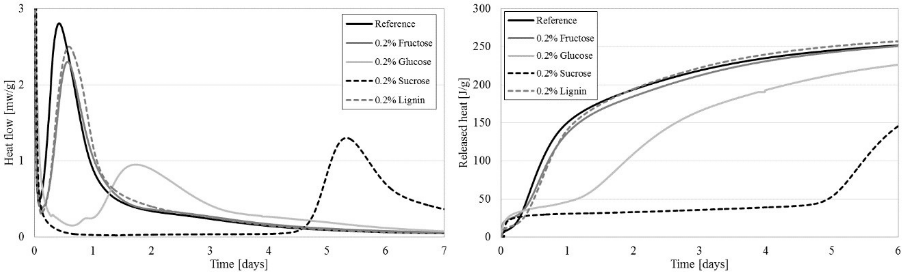
a) **b)**

Figure 3.2: Effect of 1% sugars, lignin and cellulose on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat



a) **b)**

Figure 3.3: Effect of 0.5% sugars, lignin and cellulose on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat



a) **b)**

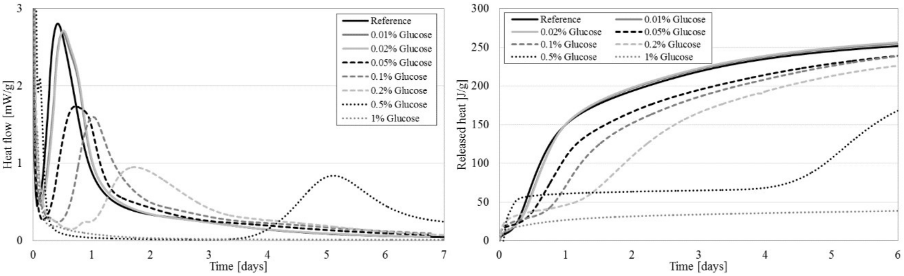
Figure 3.4: Effect of 0.2% sugars, lignin and cellulose on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

Lignin does have a strong impact on cement hydration, but the retardation is low compared to simple sugars [153]. The addition of 1% of lignin to the cement paste delays the cement hydration maximum for 63 hours (Figure 3.2a) [154]. The cement pastes with 0.5 and 0.2% of lignin was slowed down for only 10 and 6 hours, respectively.

The highest retarding effect has been observed in cement mixtures with sugars at a concentration of 1% (fructose, glucose and sucrose). No hydration was observed within the first seven days after mixing the samples.

Among the tested sugars, fructose has the lowest impact on cement hydration. The addition of 0.5 and 0.2% of fructose had a much lower impact on the maximum of the cement hydration than other sugars with the same concentrations.

Additions of 0.5 and 0.2% of glucose to the cement paste (Figures 3.2a, 3.3a and 3.4a) resulted in a retardation of the cement hydration peak of respectively five and two days. Since glucose had a significant impact on the cement hydration and knowing that glucose is often generated by cellulosic fibre in water [37,38], lower concentrations from 0.01 to 1% of glucose have also been used in this study (Figure 3.5a.). Figure 3.4b shows that the released heat after 24 hours is the same for the reference as for 0.01 and 0.02% of glucose. The relation between the glucose concentration and the retardation of the cement hydration is depicted in Figure 3.6. Moreover, the calorimetry of almost every mixture shows a first small peak after the initial wetting, indicating that the cement hydration starts with C_3S reacting before the main hydration starts [39,40]. The addition of sucrose changes the microstructure as well as the surface of the hydrating cement particles and hydration products. It caused the formation of a temporary barrier leading to further hydration [25].



a) **b)**

Figure 3.5: Effect of glucose on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

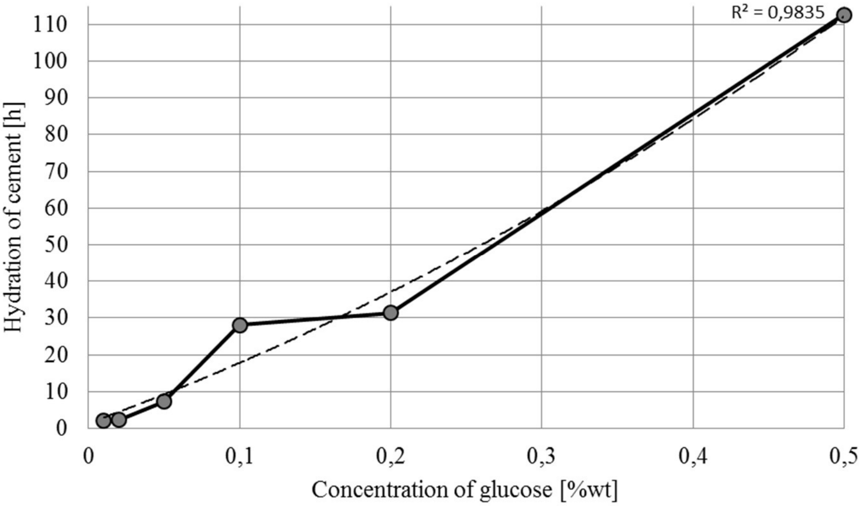
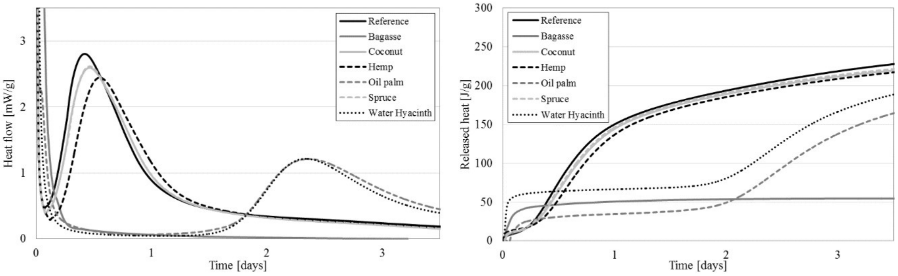


Figure 3.6: The relation between a concentration of glucose and the retardation of the cement hydration peak

Sucrose has the highest impact on the cement hydration peak (Figure 3.4a) since 0.2% of sucrose delayed the hydration for five days. Sucrose is a disaccharide combining glucose and fructose monomer units [157]. The reason for the different behaviour of the simple sugars is likely that each sugar has different stabilities in a high pH environment like cement and that they react differently with different cement minerals [112]. Sucrose is absorbed in multiple layers at cement surfaces. Cement hydration is strongly influenced by interactions between sucrose molecules and their alkaline degradation and the silicate and aluminate species at hydrating cement particle surfaces [112]. Sucrose has the most significant retarding effect at the same concentration as compared to other saccharides due to its chemical structure. It is a disaccharide and has a structure inducing a stronger steric hindrance than other saccharides [23].

3.3.2 Effect of fibre leachates on the hydration of cement

Fibre leachates were added to the cement instead of water, and calorimetry results were obtained, showing the potential influence of different natural fibres on the cement hydration (Figures 3.7a and 3.7b.).



a) **b)**

Figure 3.7: Effect of solution of fibre extractive on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

The highest retardation effect is observable with bagasse leachate, showing more than three days without any cement hydration peak. Leachates of oil palm and water hyacinth show similar behaviour, delaying the hydration maximum by approximately 47 hours. Leachate of coir and hemp had a lower effect on the cement hydration (approximately one hour delay of the hydration maximum).

As expected, the spruce leachate showed almost no retardation; it had the lowest effect on the cement hydration. This hydration peak is very close to the reference one.

3.3.3 Composition and pH of the leachates

The chemical composition of leachates was determined by HPAEC in order to evaluate the link between the leached organics and cement retardation. Table 3.3 shows the monomeric sugars concentration of the different leachates. Five monosaccharides were measured, namely arabinose, galactose, glucose, xylose and mannose. Those five monomeric sugars are the main hydrolysis products of cellulose and hemicellulose and are also components of the plant sap [150]. These monosaccharides can be found primarily in the hemicellulose structure, but the concentration of these sugars is highly dependent on the fibres.

Table 3.3: Monomeric sugars concentration in the leachates measured by HPAEC after H_2SO_4 hydrolysis and uronic acids concentration in the leachates measured by CG after methanolysis

Sample	[mg/ml]							
	Arabinose	Galactose	Glucose	Xylose	Mannose	Total sugars	GAA	GLA
Bagasse	0.24±0.02	0.39±0.03	7.4±0.33	0.61±0.03	0.56±0.02	8.65±0.43	0.07	0.74±0.01
Coir	0.21±0.02	0.08±0.01	0.04±0.01	0.56±0.05	0.02±0.01	0.91±0.1	0.02	0.07±0.01
Hemp	0.11±0.01	0.28±0.03	0.07±0.01	0.09±0.01	0.08±0.01	0.63±0.07	0.02	0.07±0.01
Oil palm	0.65±0.01	0.62±0.01	0.75±0.01	0.36±0.01	0.27±0.01	2.65±0.05	0.02	0.39±0.01
Spruce	0.03±0.01	0.04±0.01	0.03±0.01	0.12±0.01	0.07±0.01	0.29±0.05	0	0.01±0.01
Water hyacinth	0.08±0.01	0.29±0.02	0.24±0.02	0.03±0.01	0.09±0.01	0.73±0.07	0	0.13±0.01

The glucose concentration in the bagasse leachate was very high compared to other fibres (7.4 mg/ml). A high glucose content is expected because bagasse is the remaining waste from sugar cane harvested for sugar production. It also causes long retardation in the cement hydration because glucose has a very high impact on cement hydration, as shown in section 3.1, due to a disruption of C-S-H gel formation [158].

After bagasse, oil palm leachate has the highest total sugar content with 2,65 mg/l, explaining the long cement retardation. In contrast, water hyacinth leachate contains relatively low amounts of sugar (0.73 mg/l) but causes similar retardation.

Spruce wood leachate contains the lowest amount of sugars since the producers of WWCB use very simple methods to remove sugar from the wood. Logs with a length of around 50 cm are stored outside for 6 – 12 months to reduce sugar. This characteristic explains why spruce wood is commonly used as reinforcement and filler for board production.

In general, there is a good correlation between the total amount of monomeric sugars in the leachate and the total heat released during the first 3.5 days of cement hydration, which shows the degree of reaction in that time (Figure 3.8a).

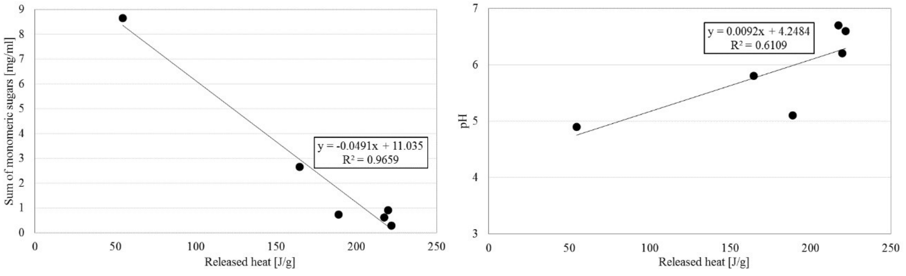
Hemicellulose is described in the literature as the primary source of monomeric sugars [159]. However, by comparing the effect of fibre leachates on the cement hydration (Figure 3.7a) and the chemical composition of fibre (Table 3.1), a high hemicellulose fraction does not correlate well with high cement retardation. It means that rather than the simple fibre composition, the nature of the leachate, i.e. its chemical composition and concentration are a better predictor.

Suppose monomeric sugars can cause a significant delay to the cement hydration due to their degradation products. In that case, the pH of the cement during the hydration phase is also a critical factor and may be affected by the numerous carboxylic acids leached by cellulosic fibres [42,45]. In order to evaluate the effect of the acid on the cement hydration, the overall pH of the leachates was measured along with two types of uronic acid (Figure 3.3) here, namely the galacturonic acid (GAA) and glucuronic acid (GLA), which are reported as the two main leached acids from natural fibre [161]. GAA is derived from galactose, and GLA is derived from glucose [162]. Table 3 depicts the selected natural fibres' leached GLA and GAA concentrations. A meagre amount of GAA has been measured in all leachates from 0 mg/ml for the spruce and water hyacinth to 0.07 mg/ml for the bagasse.

The highest GLA concentration was measured in the leachate of bagasse (0.74 mg/ml), whereas the lowest was measured in the leachate of spruce (0.1 mg/ml). Leachates of coir and hemp have the same GLA concentration (0.07 mg/ml), and water hyacinth has a slightly higher GLA (0.13 mg/ml). Table 3.4 shows the pH of all leachate solutions. Bagasse pH has the lowest pH (4.9), followed by leachates of water hyacinth and oil palm (5.1 and 5.8, respectively). Except for water hyacinth, all pH values correspond well with the amount of GLA measured, as well as the total heat released during the first 3.5 days of cement hydration (Figure 3.8b). The low pH of the water hyacinth leachate is likely caused by organic acids other than GLA and GAA, for example, levulinic and shikimic acids [163], and cause the strong retardation in the absence of high sugar concentrations in the leachate.

Table 3.4: Results of pH measurement of the leachates

Fibre	pH
Bagasse	4.9
Coir	6.2
Hemp	6.7
Oil palm	5.8
Spruce	6.6
Water hyacinth	5.1



a) **b)**

Figure 3.8: A comparison of the a) total sugar content and b) pH with the released heat after 3.5 days

Comparing the sugar leachates (Figure 3.8a) and the acid concentration (Figure 3.8b) with the normalised heat after 3.5 days shows a good correlation except for water hyacinth. Indeed, water hyacinth is known for its essential water uptake, which can significantly affect the retardation of cement hydration, as has been shown in several studies [49,50]. The correlation between total sugar content and released heat and can be used to predict the retarding behaviour of different fibres. On the other hand, the pH of the leachate (Figure 3.8b) can also be used as a fast indicator of the cement-fibre compatibility, although the correlation is less clear.

Those results suggest that a low pH is a useful indicator for a strong retarding effect. Cement paste has a pH of around 12-13, and acidic solutions could slow down the cement hydration [166] and cause a decrease of crystallinity, strength and hydration of cement [147].

3.4 Conclusion

The influence of pure saccharides and the leachates of six natural fibres on the hydration of OPC has been investigated. The following conclusions can be drawn:

- Sucrose had the highest impact on the cement hydration, while lignin and cellulose had minimal impact. At lower concentrations, fructose and lignin showed similar behaviour. The fibre composition, particularly a high hemicellulose fraction, does not appear to have a correlation with the cement hydration retardation.
- Bagasse leachate caused the longest cement hydration retardation due to the high sugar content, followed by oil palm and water hyacinth leachate. Spruce leachate had very little retarding influence due to the low sugar content.
- The total monomeric sugar content of the investigated fibre leachates corresponds well with the total heat released during cement hydration as measured with calorimetry. Those results show that the reaction of natural fibres leachates with OPC is a good way to evaluate cement/fibre compatibility. Compared to mixing natural fibres directly with OPC, it overcomes the influence of the fibre size and the water adsorption of the fibres on the reaction.
- The pH of the leachate is well correlated with the content of GLA and GAA and the total released heat during hydration. Thus, pH can be a good indicator to characterise fibre/cement compatibility in addition to other methods such as chemical analysis of the fibres and their leachate.
- In general, using isothermal calorimetry to study fibre leachates mixed with cement is an easy and cost-efficient way to investigate the compatibility of different fibres for a cement fibre composite. Using leachate prepared as described in this study allows a direct comparison without taking other factors such as fibre size or water adsorption into account. Those facts can be helpful because both properties influence the hydration behaviour of cement and can vary widely between different fibres.

Chapter 4

4 Influence of alkaline pre-treatments on alternative natural fibres used in cement-fibre composites

K. Kochova, F. Gauvin, K. Schollbach and H.J.H. Brouwers, "Influence of alkaline pre-treatments on alternative organic fibres used in cement-fibre composites," Submitted..

4.1 Introduction

Due to increasing sustainability and economic factors (e.g. renewability, recycling of wood, and less cement consumption), the use of wood has increased in past decades [2–6]. Although using wood seems to be sustainable, wood production and its transport significantly contribute to the worldwide CO_2 emission [167]. Nowadays, a large amount of organic waste, as it was mentioned previously, is generated globally, which has a vast environmental impact [8,9]. For example, the amount of coir waste is about 40 million tonnes per year in Asia [14,15]. Oil palm trees grow in more than 40 countries worldwide, producing millions of tonnes of waste every year [169]. Consequently, these waste resources can be used to develop sustainable building materials such as fibre-cement composites. Using waste natural fibres in cement composite can solve the issues related to waste or CO_2 emission, but it can also cause additional problems, especially during composite production.

Most of the natural fibres, including some types of wood, can limit the practical applications of fibres in cement composites due to the many inhibitory carbohydrates and water-soluble sugars which are leached out by the fibres and may hinder or stop the hydration of cement [17–22]. The effect of these organic retarders has been widely attributed to a mechanism based on the adsorption of extractives on the cement grains and the nucleation poisoning of hydrate surfaces [11]. Most fibres leach out the same kind of sugars, but the quality and quantity of leached water-soluble sugars depend on the fibres' nature and their growing conditions [33]. These parameters also influence the fibre's composition and microstructure, which is made of cellulose, hemicellulose, lignin, pectin, and waxes (Figure 2.11) [170]. Cellulose, one of the main constituents of natural fibre, is composed of long chains of glucose linked via glycosidic bonds. Studies show that cellulose does not have any significant effect on cement hydration because of its great resistance to degradation [25,26].

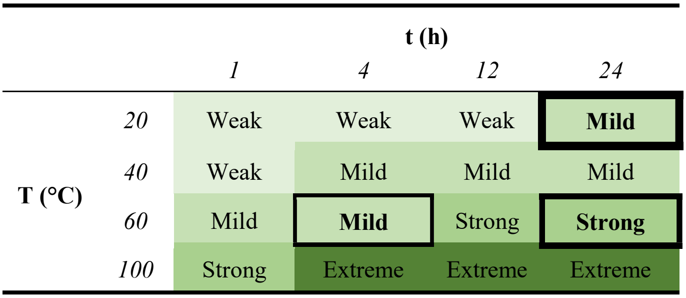
On the other hand, hemicellulose comprises different types of monosaccharides (e.g. arabinose, galactose, glucose, mannose, xylose) carboxylic acids [10], which can have a significant impact on the hydration of cement paste by decreasing the curing strength of cement. Thus, it is often necessary to remove it [11]. The third main constituent of natural fibres is lignin. It is a high molecular weight, randomly linked phenolic polymer and acts as a matrix, linking the cellulose and the hemicellulose [8]. Lignin has a complex molecular structure, and its degradation can form numerous by-products, which are mostly inert when mixed with cement paste [28,29].

Due to the problems with monosaccharides, various attempts have been made in order to improve the compatibility between cement and natural fibres, such as CO_2 injection into the cement matrix, the addition of accelerators (e.g. $CaCl_2$, $MgCl_2$, Na_2SiO_3) or fibre pre-treatments [5,30,42,31,32,35–39,41]. Chemical pre-treatments seem to be the most promising method concerning efficiency and energy-saving [32,39]. Many different conditions, such as the temperature, time or the concentration of the solution, can be found in the literature. It is known that using high temperatures and high concentrations for a long time provides the best results by removing most of the hemicellulose and sugars. However, these treatments can dramatically damage the main cellulosic structure of fibres and decrease the fibre's overall properties and thus the composite. Among the most used pre-treatments in the literature, the most effective solution is the hydrolysis of the fibre, which can be either alkaline (i.g. NaOH) or acidic (i.g. HCl).

Pre-treatments of natural fibres have been studied in the past, and alkaline pre-treatments have been underused so far. Nevertheless, alkaline pre-treatments have many advantages. They can break the hemicellulose oligomers and increase the hydrophilicity of natural fibres [131]. They can also dissolve lignin by hydrolysing acetic acids and esters [132]. Moreover, alkaline solutions are more compatible with cement. A residue of calcium hydroxide can support the cement hydration and limit the destruction of fibres' microstructure compared to other pre-treatments. Alkaline pre-treatment does not produce by-products, while acid pre-treatment does, which can influence cement hydration [28] and remove hemicellulose, lignin, wax, and oil [172].

Although the most common alkaline pre-treatment methods use sodium hydroxide (NaOH), this strong alkaline hydrolysis can damage natural fibres too much and limit their application [32,43,44]. Calcium hydroxide ($Ca(OH)_2$) is also widely available, cheap and more sustainable in comparison to the other pre-treatments. Moreover, it appears that $Ca(OH)_2$ can affect all kinds of natural fibres at a low temperature. Indeed, few studies about $Ca(OH)_2$ pre-treatment are available, and the best pre-treatment conditions are unclear [41,45,46].

From the literature [32,34,35,37,39–41,43–46], it is known that many combinations of temperature, time and concentration are possible for the chemical pre-treatments of natural fibres whose effects range from weak to extreme. This study tries to find the optimum temperature and time for a pre-treatment, which can work with various natural fibres. As described in Figure 4.1, mild and strong pre-treatments are studied in order to evaluate the effect of different conditions (i.e. time and temperature) on natural fibres. Other pre-treatments are not investigated because they are either too weak to remove inappropriate substances, which is necessary for good compatibility or too strong to destroy the fibres. Indeed, extreme pre-treatments are mainly used in the biofuel or paper industry, where the complete destruction of the hemicellulose and lignin are targeted [27,48].



		t (h)			
		1	*4*	*12*	*24*
T (°C)	*20*	Weak	Weak	Weak	**Mild**
	40	Weak	Mild	Mild	Mild
	60	Mild	**Mild**	Strong	**Strong**
	100	Strong	Extreme	Extreme	Extreme

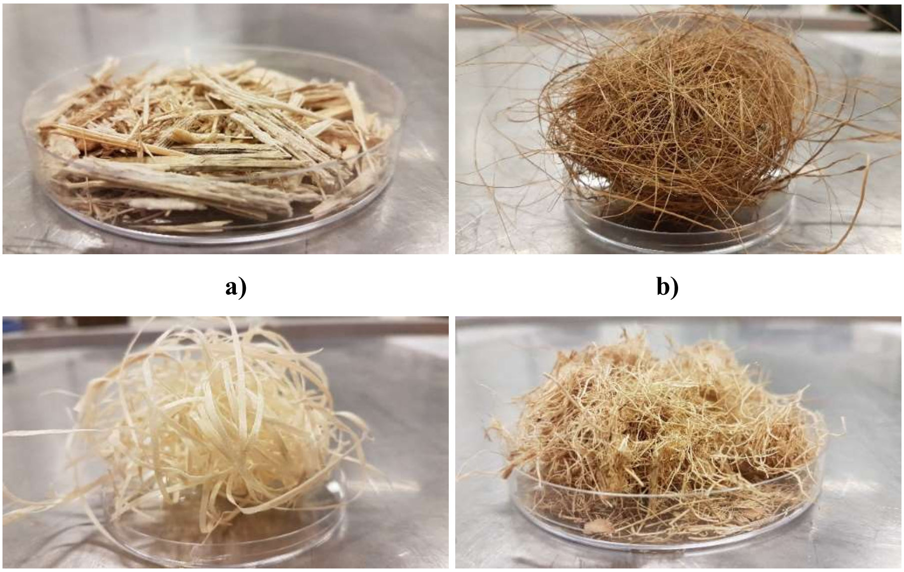
Figure 4.1: General overview of pre-treatment with $Ca(OH)_2$ and their effect on fibres

The aim of this work is to investigate the effect on bagasse, coir and oil palm waste fibres and improve their compatibility with cement in order to manufacture new kinds of cement-fibres composites. Since these fibres are known to have a more or less negative effect on cement hydration, different pre-treatments using calcium hydroxide ($Ca(OH)_2$) are performed, aiming to improve the compatibility of the fibres with cement. In-depth analyses of the fibres before and after pre-treatment are performed in order to understand the effect on the fibres. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) are used to characterise the effect of the $Ca(OH)_2$ on the surface of each fibre as well as the hemicellulose fraction. The compatibility between treated fibres and cement is determined by isothermal calorimetry followed by a method referenced by Pasca et al. [139].

4.2 Materials and methods

4.2.1 Materials

In total, four types of natural fibres are used in this study: bagasse, coir, oil palm and spruce. Bagasse, coir and oil palm – empty fruit bunch (EFB) are provided by Wageningen Food & Biobased Research, the Netherlands (Figure 4.2). Spruce wood is provided by Knauf Insulation, the Netherlands (Figure 4.2). The chemical composition of natural fibres is given in Table 4.1 [33]. Calcium hydroxide (min. 96% $Ca(OH)_2$) is provided by Merck. Ordinary Portland cement CEM I 52.5 R (OPC) from ENCI, the Netherlands, is used as a binder, and its chemical composition is given in Table 2.



a) **b)**

c) **d)**

Figure 4.2: Natural fibres: a) Bagasse; b) Coir; c) Oil palm; d) Spruce

Table 4.1: Chemical composition of the natural fibres measured by HPAEC after H_2SO_4 hydrolysis [33]

		Fibres			
		Bagasse	**Coir**	**Oil palm**	**Spruce**
Cellulose	[%]	34.2	36.6	32.8	41.6
Hemicellulose		40.1	37	42.7	37.3
Lignin		11.9	22.2	14.9	19.4
Ash		3.9	1.9	7.8	0.4
Extractive		13.8	4.2	8.6	1.7

Table 4.2: Chemical composition of ordinary Portland cement CEM I 52.5R used in this study

Chemical composition	**[%]**
CaO	64.60
SiO_2	20.08
Al_2O_3	4.98
Fe_2O_3	3.24
K_2O	0.53
Na_2O	0.27
SO_3	3.13
MgO	1.98
TiO_2	0.30
Mn_2O_4	0.10
P_2O_5	0.74
Cl^-	0.05

4.2.2 Methods

4.2.2.1 Pre-treatment

A saturated solution of $Ca(OH)_2$, close to pH 12, is prepared. Fibres are dried at 60°C prior to pre-treatment. They are then soaked in the saturated solution of $Ca(OH)_2$ at three different conditions; 24h/20°C, 4h/60°C and 24h/60°C. Fibres are then washed several times and dried at 60°C.

4.2.2.2 FT-IR

Fourier Transform Infrared Spectroscopy (FT-IR) spectra are recorded using a Perkin Elmer Frontier FTIR with a GladiATR diffuse reflectance device. Eight scans are acquired with optical retardation of 0.25 cm and a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}. This method is used to characterise the effect of the pre-treatments on hemicellulose at the surface of the fibre. The peak at 1730 – 1750 cm^{-1} corresponds to C=O groups, characteristic of the carboxylic acid of hemicellulose [25,40], which is measured for both untreated and treated fibres.

4.2.2.3 SEM

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses are performed using a Phenom Pro X scanning electron microscope to observe the surface of untreated and treated fibres in order to study the degradation of the fibres after pre-treatments. Micrographs are recorded using both scattering electron detectors at 15 kV with a spot of four.

4.2.2.4 Mass loss

Fibres are dried and weighed before pre-treatments. After pre-treatments, the fibres are washed twice to remove calcium hydroxide and sugars. Filter papers (⌀ 120 mm) are used to prevent the loss of the fibres. The treated fibres and the filtered paper were dried at 105°C and weighted. Then, the mass loss is calculated and compared for each treated fibre. This method allows observing the evolution of the fibre's mass during pre-treatment due to the elimination of sugars, wax and oil.

4.2.2.5 Water absorption

Water absorption (WA) measurements aim to determine the amount of water absorbed by each fibre when they are soaked in water for 24h at room temperature. Prior to measurement, the fibres are dried at 105°C for 24 hours. This method is applied six times for each fibre, with and without pre-treatment. The WA is calculated using an equation

$$\mathrm{WA} = \frac{\mathrm{mw-md}}{\mathrm{md}} * 100 \tag{4.1}$$

where: m_w is the fibre after soaking in water; m_d is the dried fibre

4.2.2.6 Isothermal calorimetry

Isothermal calorimetry is performed with a TAM Air Isothermal calorimeter at a constant temperature of 20°C. All untreated and treated fibres are mixed with OPC and water. The water/cement ratio is kept constant for all prepared mixes (w/c = 0.45), and the fibres/cement ratio was 0.075. An average of 36g of the mixture is used for one sample, with a particle size of the fibres 2 – 4 mm.

4.2.2.7 Cement-fibre compatibility

Several authors [18,21,22,50] have formulated different methods to measure the compatibility of wood species with OPC. In this study, an equation designed by Pasca et al. is used to assess the compatibility CX' between different natural fibres and the OPC [139]. The equation is developed for cement-wood compatibility but can be suitable for other natural fibres used in this study. Due to the assumption that hydrated cement/wood/water mixtures and cement/fibres/water mixtures tend to have the same cement hydration behaviour as they have similar chemical composition [139].

The CX' factor can be determined using the equation [139]:

$$\mathrm{CX'} = \sqrt[3]{\left(\frac{\mathrm{HRmax*HR3.5-2\ \ *t'max}}{\mathrm{HR'max*HR'3.5-24*tmax}}\right)} * 100 \tag{4.2}$$

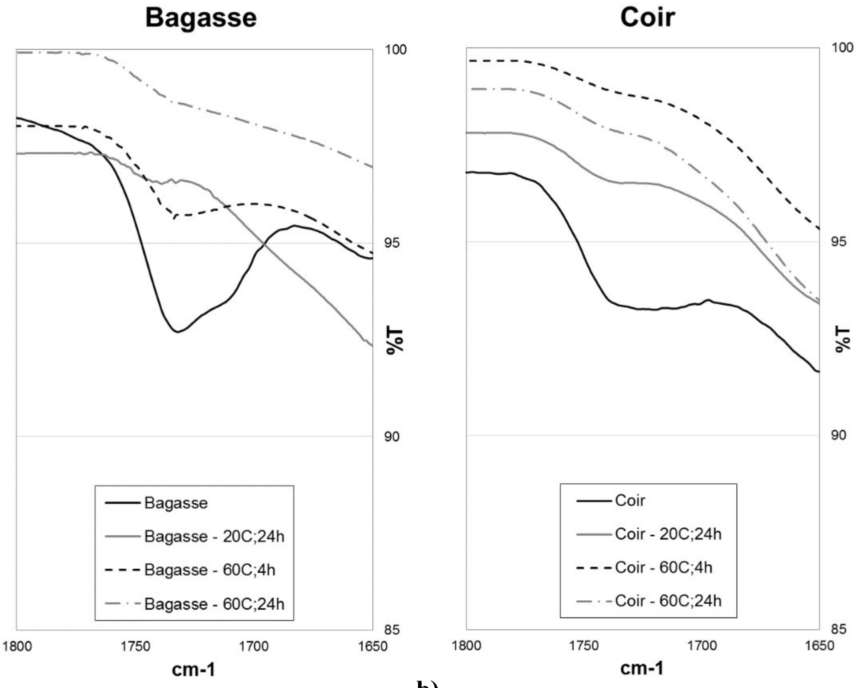
where HR_{max} is the maximum heat rate of cement wood mixtures; $HR_{3.5-24}$ is the total heat released by cement wood mixtures in its hydration period (3.5 – 24 h); t_{max} is the time to reach maximum heat rate of cement mixtures; HR'_{max} is the maximum heat rate of neat cement mixtures; $HR'_{3.5-24}$ is the total heat released by neat cement mixtures in the hydration period; t'_{max} is the time to reach maximum heat rate of neat cement mixtures. All the calculations were based on the mass of the mixture. Three borders can be defined to classify cement-fibre compatibility: Incompatibility: $CX' < 40$; moderate compatibility: $40 \leq CX' \leq 80$; compatibility: $CX' > 80$.

4.3 Results and discussions

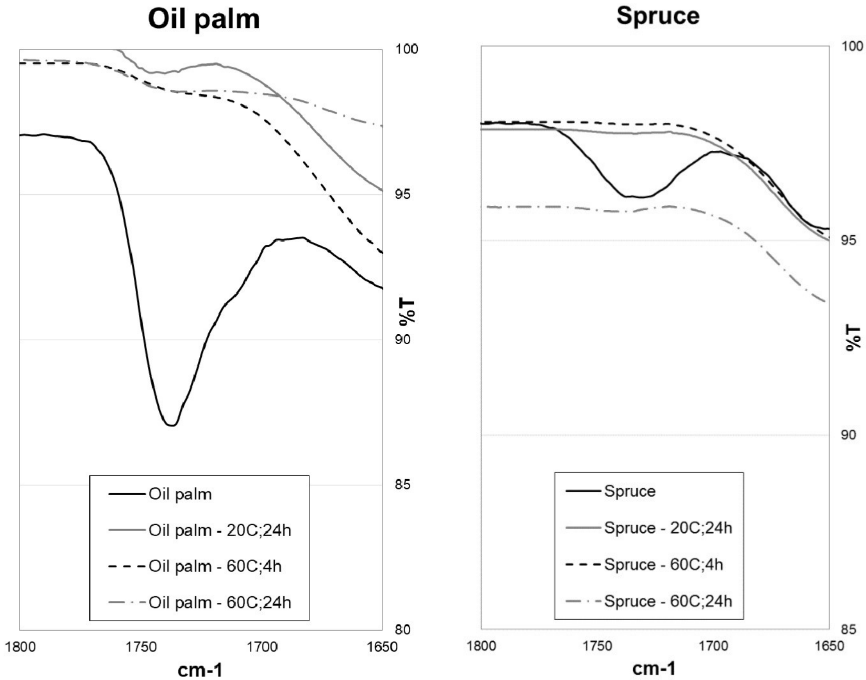
4.3.1 Composition of fibres

FT-IR spectroscopy can give qualitative insight into the composition of lignocellulosic materials. In this study, the bending vibration of C=O groups is measured at 1730 – 1750 cm^{-1}, which corresponds to the hemicellulose (the only constituent of a natural fibre made of carboxylic acid, ketone and aldehyde bonds) [25,51]. Moreover, the investigation of the hemicellulose in the fibres is interesting in this study because hemicellulose is known to be the major cause of cement hydration delay when the natural fibres are mixed with cement [33].

Figures. 4.3a – d summarise the effect of the pre-treatments on the hemicellulose bands observed by FT-IR of all fibres. Before pre-treatment, the bagasse fibres show a very strong peak, which almost disappeared after being pre-treated. Similar results can be observed with mild (4h/60°C) and strong (24h/60°C) conditions. Analyses of oil palm fibres (Figure 4.3c) show very similar results.



a) b)



c) d)

Figure 4.3: FT-IR spectra 1800 – 1650 cm^{-1} of a) Bagasse, b) Coir, c) Oil palm and d) Spruce fibres used different pre-treatments

The coir and the spruce fibres have less hemicellulose in their structure than bagasse and oil palm fibres (Table 4.1), which results in removing less hemicellulose during the pre-treatments than with other fibres. The intensity of the hemicellulose peak of the coir fibres (Figure 4.3b) decreases significantly after pre-treatment at 60°C, regardless of the pre-treatment duration. After pre-treatments of spruce, the peak corresponding to the hemicellulose entirely disappeared (Figure 4.3d).

From Figures 4.3a – d, it is clearly seen that the fibres' structure is changed, and the hemicellulose is partly or entirely removed. One of the most visible differences is between the untreated and treated fibres with the strong pre-treatment. Moreover, some similarities of the structure with a couple of the fibres are observable: The FTIR spectra of hemicellulose for the treated coir and spruce fibres were similar, as well as the treated bagasse and oil palm fibres.

4.3.2 Surface of fibres

A surface characterisation analysis is performed to evaluate the effect of each pre-treatment with each fibre. Figures. 4.4 – 4.7 present the surface morphology of the untreated and the treated fibres obtained by Scanning Electron Microscopy. A comparison between the untreated and the treated bagasse fibres (Figures 4.4a – d) shows that the untreated bagasse fibre had a smoother and uniform surface. The pre-treatments with high temperature (60°C) and washing led to morphological changes due to removing compounds like extractives and wax (Table 4.1).

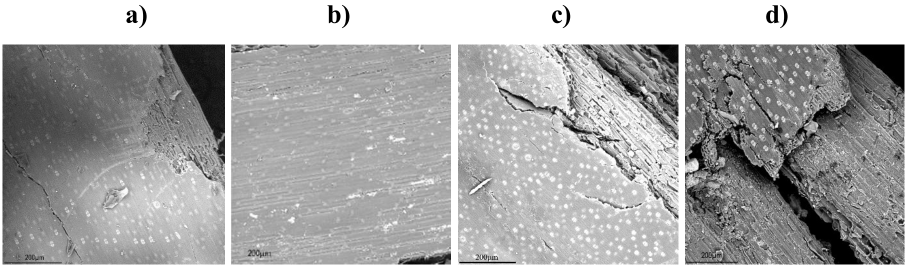


Figure 4.4: SEM pictures of bagasse fibres

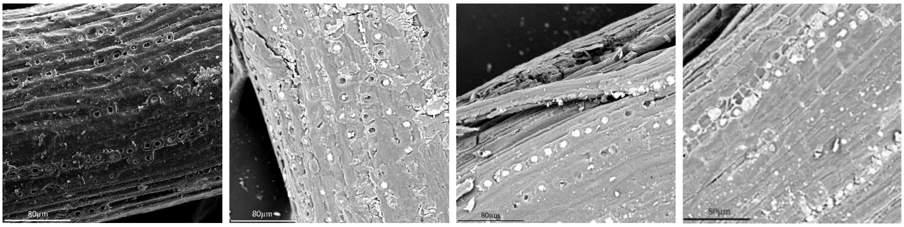


Figure 4.5: SEM pictures of coir fibres

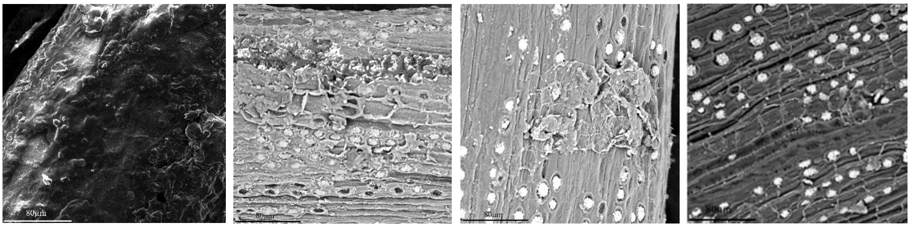


Figure 4.6: SEM pictures of oil palm fibres

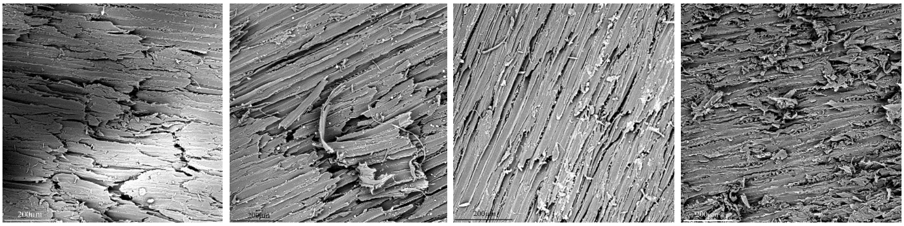


Figure 4.7: SEM pictures of spruce fibres

The coir and the oil palm fibres show a very different morphology than other fibres. A thick layer covers the fibres, which appears, from the literature [34,52,53], to be wax and oil (Figures 4.5a and 4.6a). Figures 4.5d and 4.6d show that the strong pre-treatment can remove them from the surface of these two fibres. Moreover, at higher magnification, traces of unknown micrometric particles can be noticed inside the pores of these fibres. EDX analyses of the oil palm fibre (Table 4.3b) determined that these particles are silica-based, which seems to normally occur in oil palm fibres as a biological process and simultaneously helps with the strength and rigidity of fibres

[54,55]. With the treated coir fibre, EDX characterisation (Table 4.3a) shows that the particle inside the pores is calcium-based, which could be caused by an insufficient washing after the pre-treatment where the same amount of water was used for all treated fibres. The silica-based structure was also found in the coir fibres but only in a small amount compared to the oil palm fibres [181].

Table 4.3: Semi-quantitative EDX characterization: a) Coir fibre; b) Oil palm fibre

	Element Name	Atomic Conc.
a)	Carbon	60.3
	Oxygen	37.1
	Calcium	2.7
b)	Carbon	62.1
	Oxygen	32.4
	Silicon	5.4

As shown in Figure 4.7, the treated spruce fibres do not show significant changes on the surface. By comparing Figures 4.7a and 4.7d, it appears that the surface is slightly rougher after the pre-treatment. Pre-treatments can remove hemicellulose, wax, and oil as well as roughen the surface, which can be seen in Figures 4.4 – 4.7. The modified surface (i.e. different roughness and presence of calcium residues) could be helpful during the board production due to a better interaction between cement and fibres.

4.3.3 Mass loss

The mass loss of each fibre is measured to confirm the effect of the pre-treatments on the dissolution and elimination of hemicellulose, lignin and other substances from the fibres. Figure 4.9 shows the results and allows the comparison between pre-retreatments, as well as fibres themselves. Two groups of fibres can be differentiated.

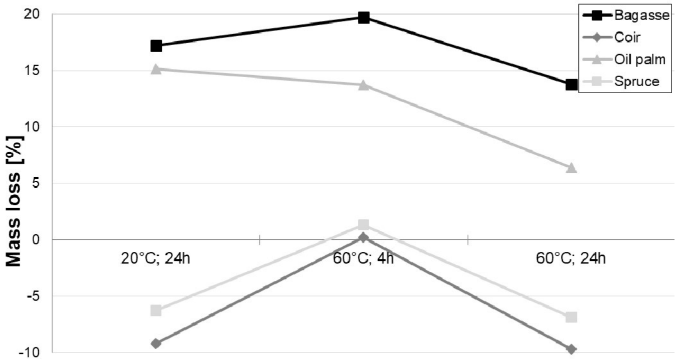


Figure 4.8: Mass loss of treated fibres with different pre-treatment conditions

With the first group, the oil palm and the bagasse fibres, a significant weight loss is observed (up to 20%). As expected, the strong pre-treatments causes a more significant mass loss for both fibres. These fibres also have a similar composition (Table 4.1), with high hemicellulose and extractive content. The bagasse has the highest mass loss between them due to its extremely high extractive content.

With the second group, the spruce and the coir fibres, the trend is very different, where both fibres gain weight after pre-treatments and drying at 105°C. It also appears that the pre-treatment conditions have an influence on the mass loss, and the long (24h) pre-treatments lead to more important weight gains (up to + 10% with the coir fibre). This phenomenon could be a result of remaining Ca on the surface (Figure 4.9, Table 4.3a) and Ca penetrating to pores when silica bodies are removed (Figure 4.5b,c and d), which eventually crystallised after drying as well as swelling reaction of the fibres on the alkali pre-treatment [57,58].

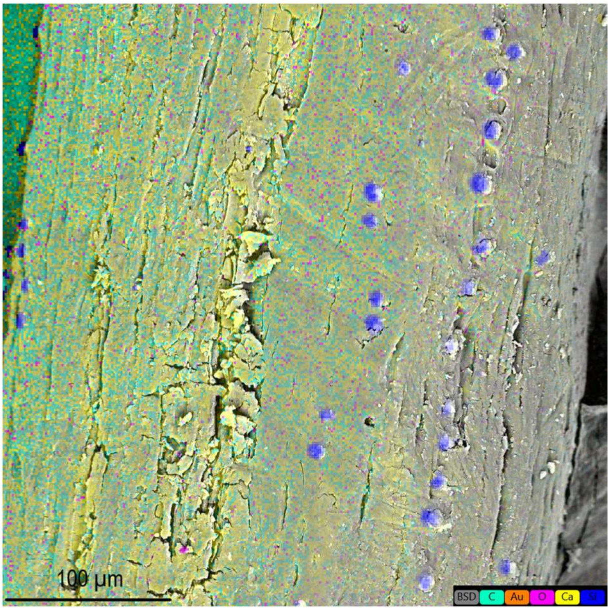


Figure 4.9: SEM pictures and EDX of coir fibre (pre-treatment at 60°C for 4h)

Finally, a correlation between the mass loss after the pre-treatments (Figure 4.8) and the chemical composition of the fibres (Table 4.1) is observable, notably with lignin and cellulose: When the lignin content increases, the mass loss decreases, and the opposite effect is seen with the cellulose. This phenomenon can be explained by the hydrophilic behaviour of cellulose and the hydrophobic behaviour of lignin [10], where lignin can be considered as a shield protecting the fibres. A similar trend can be seen with the extractive, where increasing the extractive of fibres increases the mass loss.

4.3.4 Water absorption

Figure 4.10 depicts the untreated and treated fibres' water absorption (WA) measurements. WA is important in the production of cement-fibre composites due to an intake of the water available for cement hydration by the fibre during 24 hours.

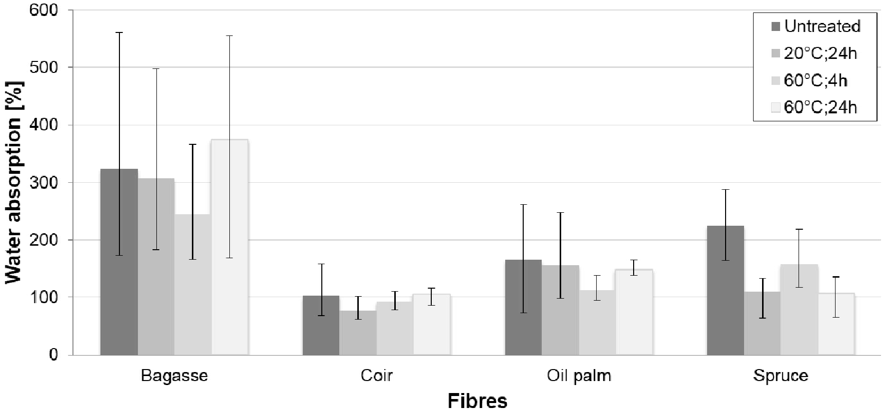


Figure 4.10: Water absorption of untreated and treated fibres

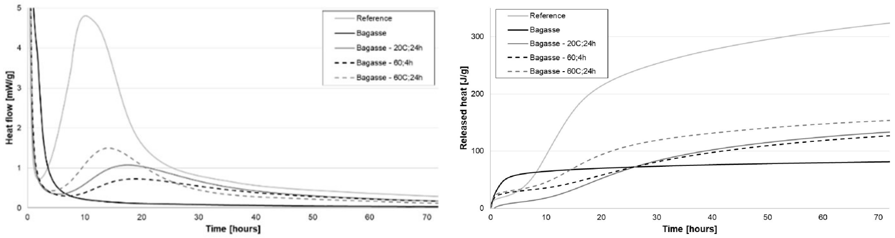
As expected, the bagasse fibres have the highest WA of the examined fibres due to their porosity and chemical composition (Table 4.1). Its hemicellulose and cellulose content is the highest among all the tested fibres. It is known that hemicellulose and cellulose are hydrophilic, and the bagasse can absorb a high amount of water [184]. The oil palm fibres also have a high amount of hemicellulose and cellulose, but the WA is lower, mostly due to the wax layer all around the fibres (Figure 4.6a). The coir fibres have the lowest WA on account of the high lignin content (Table 4.1), which is hydrophobic [10] and the spruce fibres.

In general, any pre-treatment decreases the WA of the fibres, except for the bagasse after a strong pre-treatment (the WA increases by 16%). This phenomenon can be caused by the heterogeneity of this fibre (i.e. raw bagasse fibres are constituted of two parts; the surface and the inner part, which is very porous), as seen in Figure 4.2a. The bagasse, coir and oil palm fibres follow a similar trend. After the mild pre-treatment, the fibres have a lower WA than the fibres, which have undergone a strong pre-treatment. Those pre-treatments change the surface properties, as well as the amount of available hemicellulose, which dramatically influences the WA. Decreasing the cellulose and hemicellulose content in the fibres causes a relative increase in the lignin content, and the fibres become more hydrophobic. Furthermore, the combination of the residue of $Ca(OH)_2$ on the surface of the fibres can change the WA behaviour (decreasing WA) by closing pores (Figure 4.10).

From the previous results, two groups of fibre can be differentiated. The first group (coir/spruce) consists of fibres with a smooth surface (Figures 4.5a and 4.7a), low extractive amount and relatively high lignin content. After removing wax with the pre-treatments, the second group (bagasse/oil palm) shows a higher surface roughness. Both fibres have a high amount of extractive and low lignin content. Using the pre-treatments change the hemicellulose content, as well as the surface of the fibres. Meaning the wax is removed, and the surfaces are rougher than before the pre-treatments.

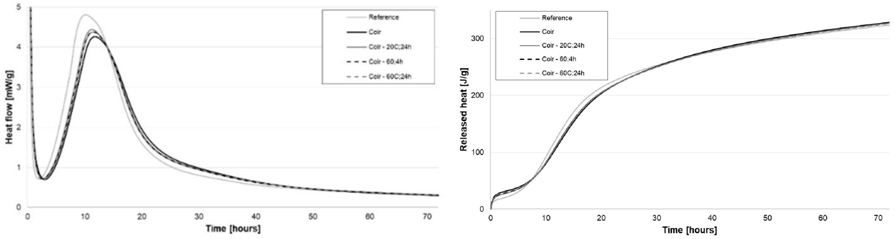
4.3.5 Cement-fibre compatibility

The untreated and the treated fibres are added to the cement paste and tested by isothermal calorimetry in order to study the influence of the different pre-treatments on the cement hydration of cement/fibre mixes (Figures 4.11 – 4.14).



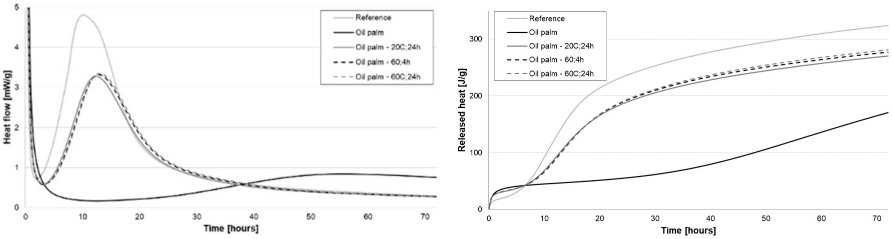
a) b)

Figure 4.11: Effect of bagasse fibres after and before pre-treatment on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat



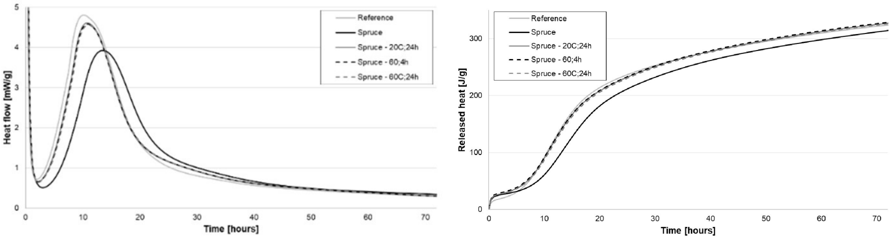
b) b)

Figure 4.12: Effect of coir fibres after and before pre-treatment on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat



c) **b)**

Figure 4.13: Effect of oil palm fibres after and before pre-treatment on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat



d) **b)**

Figure 4.14 Effect of spruce fibres after and before pre-treatment on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

As seen by FT-IR and the mass loss analysis, coir and spruce fibres exhibit a similar behaviour during pre-treatment. Calorimetry shows that they both have little or no influence on the cement hydration before and after pre-treatments (Figures 4.12, 4.14). The released heat after 72h (Figure 4.12b) is the same for the reference (OPC) and the untreated and the treated coir fibres. The cement hydration peak is delayed for two hours for the untreated spruce fibres, and the released heat is lower. Using pre-treatments removes the delay of the cement hydration peak, and the released heat after 72h is the same as with OPC (Figures 4.14a and b). Figures 4.11a and b depict the untreated and the treated bagasse fibres and their retardation effect on the cement hydration. The addition of untreated oil palm fibres to the cement paste (Figures 4.13a and b) results in retardation of the cement hydration peak for more than one day, but pre-treatments at 60°C seem to solve this problem.

By using the isothermal calorimetry measurements (Figures 4.11 – 4.14) and Pasca's equation (4.2), the cement-fibre compatibility is calculated for each fibre and depicted in Table 4.4.

Table 4.4: Cement-fibre compatibility of ordinary Portland cement CEM I 52.5R and untreated and treated fibres

Fibres	Untreated	Pre-treatments		
		20°C; 24h	*60°C; 4h*	*60°C; 24h*
Bagasse	0	43	34	49
Coir	88	89	88	89
Oil palm	13	76	78	78
Spruce	87	88	88	88

The highest improvement is observed with the oil palm fibres, where the pre-treatments increase the compatibility from 13 (incompatible) to more than 78 (moderate compatibility), regardless of the pre-treatment conditions. A good improvement is also seen with the bagasse fibres, where the compatibility with the untreated fibres is calculated to be 0. Still, with a mild pre-treatment, a significant improvement is seen (34 – 43). With a strong pre-treatment (24h/60°C), the compatibility increased up to 49 (moderate compatibility), which is still not good enough for the production of the cement-fibre boards but is a great improvement for a fibre which had currently too problematic to be used in cement composites.

As mentioned before, spruce fibres are not known to disrupt the cement hydration of OPC significantly. This property is characterised by calculated compatibility of 87, which is compatible. The pre-treatments increase the compatibility slightly (88), which can be explained by eliminating some hemicellulose, which is shown in Figures 4.3d and 4.7b – d. Similarly, even without pre-treatments, the coir fibres show good compatibility with OPC (88, 89), which is equal to spruce. The compatibility is slightly better after pre-treatment (24h). Nevertheless, micrographs (Figure 4.5a) show that after pre-treatments, the coir fibre surface is modified, meaning that the pre-treatments do have an impact but do not affect the hydration, thus the compatibility.

The fibres have a similar chemical composition as is shown in Table 4.1; nevertheless, the effect on cement hydration and the cement fibre compatibility is different. This phenomenon can be explained by the extractive content (which is known from the literature to be mostly by-products of the hemicellulose degradation) is significant and has a strong effect during the hydration behaviour of the cement-fibre mix [23,[147],[150].In this study, the chosen pre-treatments are either mild (24h/20°C, 4h/60°C) or strong (24h/60°C), as shown in Figure 4.1. One hypothesis is that strong pre-treatment would lead to better cement-fibre compatibility. However, from the compatibility results (Table 4.4), it appears that strong pre-treatments have the same effect as mild pre-treatments on all the fibres. Nevertheless, the strong pre-treatments are unnecessary except on bagasse fibres unless fibres are mostly made of extractive and hemicellulose. However, SEM micrographs (Figures 4.4d – 4.7d) show that the strong pre-treatment degrades the fibre more than the mild pre-treatments even though no benefits are observed from a compatibility point of view. From these results, coir and the oil palm fibres are promising candidates for the board industry. Indeed, looking at their compatibility results, coir fibres are compatible, and the oil palm fibres are moderate compatible. Moreover, SEM characterisation shows that the pre-treatments remove wax from the surface of the oil palm and increase the surface roughness of both fibres, which can help to improve bonding between cement and fibres.

From the previous results, it seems that the effects of the strong pre-treatment are mostly on the surface of the fibres (spruce, coir fibres), and the compatibility is nearly the same. This effect could be due to the solid fibres (long, unbroken fibres with a small diameter), where hemicellulose and other substances are removed from the surface. At the same time, it can be seen the improvement of the compatibility with oil palm and bagasse fibres.

4.4 Conclusion

The influence of pre-treatments with $Ca(OH)_2$ on four different natural fibres, as well as their compatibility with OPC, were investigated. Three conditions, namely two mild pre-treatments (24h/20°C, 4h/60°C) and a strong pre-treatment (24h/60°C), were chosen to optimise the pre-treatment conditions with saturated $Ca(OH)_2$. The following conclusions can be drawn from the present study

- Two groups of fibres can be identified through the experiments based on their similar behaviour. The first group consists of the coir and spruce fibres, and the second of the bagasse and oil palm fibres. These fibres have similar hemicellulose and extractive contents but different microstructures, showing that the chemical composition significantly influences cement-fibre compatibility.
- Pre-treatments have almost no effect on fibres' CX factors from the first group (i.e. spruce and coir fibres). This result is expected because both fibres are considered compatible before pre-treatments (CX' = 87 and 88, respectively). On the other hand, after pre-treatments, the CX' factor of fibres from the second group (i.e. bagasse and oil palm fibres) increased significantly, making these fibres much more compatible
- Pre-treatment conditions (time and temperature) have a limited effect on the CX' factor, meaning that the mild pre-treatments (24h/20°C and 4h/60°C), as compared with strong pre-treatment (24h/60°C), are efficient enough to improve the compatibility between cement and most of the fibres. Nevertheless, bagasse fibres need a strong or even extreme pre-treatment in order to increase the compatibility due to a high amount of hemicellulose and extractive, which are the highest among the tested fibres.

The CX' factor is not the only important factor to assess cement-fibre compatibility. Indeed, physical properties like surface roughness or water absorption can also affect the processing of cement-fibre composites. From this study, it appears that pre-treatments can remove hemicellulose from the surface and increase the roughness of fibres. The changes in the structure of fibres result in a change of the WA, which will eventually lead to important modification of the mix design of cement-fibre boards.

Chapter 5

5 Investigation of local degradation in wood stands and its effect on cement wood composites

K. Kochova, V. Caprai, F. Gauvin, K. Schollbach, and H.J.H. Brouwers, "Investigation of local degradation in wood stands and its effect on cement wood composite," Constr. Build. Mater., vol. 231, 117201, 2019

5.1 Introduction

The popularity of natural material is mainly related to the increasing concerns about sustainability in the building industry [185]: Natural fibres are not expensive and have lightweight, non-toxic and biodegradable properties that lead to many applications as replacement of synthetic fibres [186]. One commonly used composite is the wood wool cement board (also called Excelsior board, WWCB), produced using Spruce (*Picea Abis*) wood wool strands, white cement and chemical [1,5,6]. Having a thickness between 50 and 150 mm, WWCBs are mainly applied as ceiling tiles for acoustic insulation. Still, they also have good acoustic properties and durability against fungi thanks to fibre mineralisation [1,2,7]. Due to the numerous critical factors affecting the wood quality, WWCB production has to consider several aspects during the board manufacture: Geometry and mechanical strength of the wood strand, their water adsorption, wood/cement ratio, and general wood cement compatibility [11]. Among the influencing factors, low wood cement compatibility plays a significant role in WWCB performances [189]. The presence of leachable extractives is known to delay the cement hydration, leading to the composites' low strength [33,190,191]. For these reasons, industrial WWCB production relies mostly on conifers such as pines or spruce wood from commercial forests [192], characterised by a minimal presence of leachable extractives [8,10,18].

Moreover, after felling, the trunk is cleaned from the bark and stored as logs for 6-12 months to reduce the moisture content and limit the presence of those extractives [10,13]. Consistent moisture content and water absorption of the wood are important aspects because cement requires a specific water/cement ratio in order to hydrate and provide adequate strength, typically 0.35-0.5 [5,6]. If the moisture content of wood is too high, it can release the water and increase the effective water/cement ratio, leading to a porous binder with low strength [5,16]. It is also possible that the wood absorbs too much water needed for cement hydration. In that case, part of the cement cannot hydrate, which also leads to the low strength of the composite [5,14].

Even if these factors are taken into account, wood is a natural material, and its properties can vary even within the same species [8,17]. Therefore, consistent and strict quality control is essential prior to composite manufacture. However, even with this assessment, some batches of wood can perform poorly in WWCB. It leads to defective boards with either insufficient flexural strength (minimum required by the standard BS EN 12089 - 1.7 MPa [197]) or swelling/loss of cohesion of the boards after demoulding. The reasons for these failures are still poorly understood and few studies about bad quality wood and its effects on the overall performances of WWCB exist.

This study focuses on two different wood samples, named wood A and wood B, in order to investigate their effect on WWCB. The batches of spruce wood were grown and cut in the exact European location. One of these two batches (B) resulted in low quality during the industrial manufacture of WWCBs, even though it passed quality controls. First, WWCBs are manufactured with these two types of wood in order to compare their flexural strength and density. Then, the wood strands are mixed with white cement, and by using isothermal calorimetry, the compatibility of the two types of wood with cement is assessed. After that, the mechanical strength of individual wood strands is tested to determine the influence of wood quality on fibre and board performances. Microscopy at the wood surface but also inside the pores aims to confirm the previous observations. Finally, wood leachates are prepared and analysed by anion exchange chromatography to compare their polysaccharides concentration.

5.2 Materials and methods

5.2.1 Materials

In this study, two types of spruce wood wool were collected from an industrial manufacturer of WWCBs and are named wood A and wood B. The wood wool is approximately 1 - 3 mm in width, 0.1 - 0.5 in thickness and 25 cm in length [192]. The average chemical composition of the spruce fibres is given in Table 5.1. White cement CEM I 52.5 R from ENCI, the Netherlands, is used as a binder, and its chemical composition is shown in Table 5.2.

Table 5.1: Spruce wood strands chemical composition as measured in a previous study [33]

Chemical composition	**[%]**
Cellulose	41.6 ± 0.1
Hemicellulose	37.36 ± 1.1
Lignin	19.46 ± 1.1

Table 5.2: Chemical composition of white cement CEM I 52.5R white used in this study

Chemical composition	[%]
CaO	62.21
SiO_2	20.93
Al_2O_3	3.90
Fe_2O_3	0.45
K_2O	0.12
Na_2O	0.11
SO_3	2.92
MgO	0.43
TiO_2	0.33
Mn_3O_4	0.02
P_2O_5	0.51

5.2.2 Methods

5.2.2.1 Manufacture of the composite

Wood wool cement composites are manufactured based on the dry method, commonly applied by composite manufacturers. The spruce strands (1-3 mm in width, 0.1-0.5 in thickness and 25 cm in length) are pre-soaked with water until they reach a certain moisture content, and thereafter dry binder is sprinkled on them. After mixing, the wood-binder mixture is placed in a mould (30 x 20 x 1.5 cm) and pressed for 24 h under a mechanical press. Afterwards, the board is cured in plastic sheets for seven days and left at ambient conditions for three days. Finally, the board is dried at 50°C for 2 h prior to mechanical testing. The water to binder ratio used in this study is 0.5, while the wood to binder ratio is 0.75.

5.2.2.2 Mechanical performances

Mechanical performances of the WWCB are tested by a three-point bending test (Zwick 2020) following the BS EN 12089, *Thermal insulating products for building applications* standard on a sample 20 x 15 x 1.5 cm, using a testing speed of 1.5 mm/min and a support span of 15 cm (method A) [197]. As reference values, the standard indicates that a board is acceptable with a maximum thickness of 1.5 cm, a minimum bending strength of 1.7 MPa and a density of 500 – 600 kg/m^3.

5.2.2.3 Isothermal calorimetry

Isothermal calorimetry is performed by using a TAM Air Isothermal calorimeter at a constant temperature of 20°C. Fibres with a 2 – 4 mm particle size are mixed with cement and water. The water/cement ratio is kept constant for all prepared mixes (w/c = 0.45) and the fibre/cement ratio is 0.075. After mixing, the samples are placed in the calorimeter with a large cup holder (i.e. 40 g of materials can be tested) to observe and determine the cement hydration behaviour.

5.2.2.4 Compatibility

This study uses an equation by Pasca et al. [139] to assess the compatibility CX' between wood fibres and cement. The equation is developed for cement-wood compatibility, and it used cement/wood/water mixtures to calculate the compatibility. The CX' factor can be determined using equation (4.2) [139].

5.2.2.5 Tensile properties of wood strands

Mechanical properties of wood strands are measured using an Instron 5967 bench equipped with a 2530-100 N load cell and a 2710-111 wedge grip with rubber jaw faces. Tensile tests are conducted in displacement control with a 5 mm/min crosshead speed. More than 15 samples were tested. Tensile strength (cN/tex) and Young's modulus (N/tex) are measured as a function of the linear density of the fibre (tex) by measuring the length and the weight of each fibre prior to analysis.

5.2.2.6 Scanning electron microscopy

SEM analyses are performed by using an FEI quanta 600 environmental scanning electron microscope to observe the surface and the cross-section of the wood. Micrographs are recorded by using both secondary and backscattering electrons detectors at 10 kV with a spot of 4 in low vacuum mode (0.6 mbar).

5.2.2.7 Leachate preparation

Wood samples are dried at 60°C to constant mass and soaked for 2 hours at 100°C in distilled water (water/fibres ratio = 5:1). Filtrate and fibres are separated with filter paper. The pH of the fibre leachates is measured by a pH Meter (Metrohm 780) at room temperature.

5.2.2.8 The concentration of monomeric sugars and uronic acids

The concentration of the monomeric sugars of the different leachate solutions is determined by high-performance anion-exchange chromatography (HPAEC) after H_2SO_4 hydrolysis. The solution is freeze-dried (1 – 4 ml of leachates) and vigorously mixed in Pyrex test tubes with 150 µl of ice-cold H_2SO_4 (12 mol.L^{-1}) in a water bath at 30°C for one hour. Samples are then removed from the water bath and mixed with an H_2SO_4 (4%) solution. Samples are then placed in an autoclave for 60 min at 120°C. After being cooled down, 5 mg of ribose is added to each sample as an internal standard. Prior to analysis, hydrolysed leachates are diluted with deionised water at a different ratio (from 1:10 to 1:100). Measurements are done with a Thermo Scientific

Dionex ICS-5000 system. Samples are separated on a Dionex CarboPac PA1 carbohydrate column.

The concentration of uronic acids is then measured by gas chromatography (GC) after methanolysis, according to Sundberg [151]. Samples are lyophilised and then hydrolysed in 2 M methanolic HCl at 100°C for 5 h, followed by the addition of pyridine and sorbitol as an internal standard at room temperature. After evaporation under N_2, samples are silylated overnight with HMDS (hexamethyldisilazane, Sigma-Aldrich) and TMCS (trimethyl-chlorsilan, Sigma-Aldrich) in pyridine, injected into a GC/FID system (7890A, Agilent Technologies) at 260°C, and separated on an HP-5 column (30 m, 0.32 mm ID, 0.25 µm film thickness) using the following temperature program: 150°C for 1 min, 150°C to 220°C at 4°C/min, 220°C to 320°C at 20°C/min, 320°C for 6.5 min. Calibration of peak areas is done using identically treated authentic standards of D-glucuronic and D(+)-galacturonic acids.

5.3 Results and discussion

5.3.1 Mechanical performances of the wood wool composites

The WWCB mechanical performances are displayed in Figure 5.1, together with the relative board density. It appears that their flexural properties are significantly different. Wood A surpasses Wood B by three times, reaching almost five MPa flexural strength. Moreover, due to the low performance of WWCB, Wood B does not fulfil the minimum requirements necessary for boards 1.5 cm thick [198] and are therefore not eligible for application.

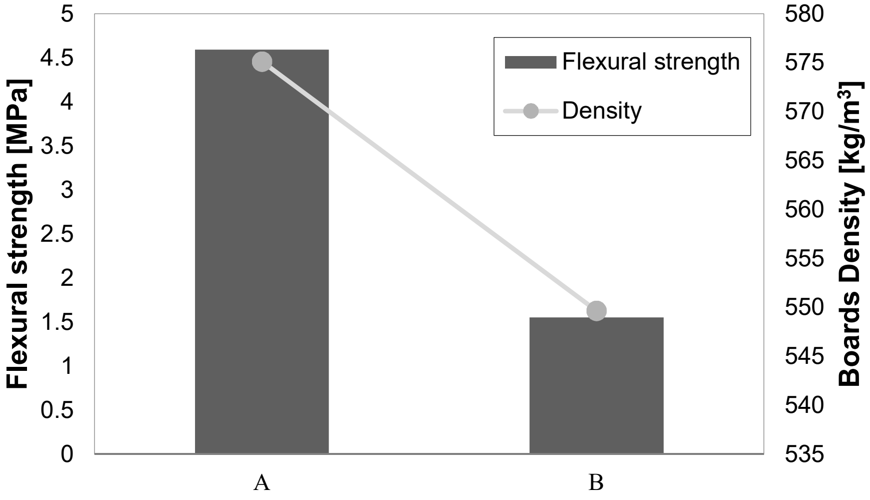
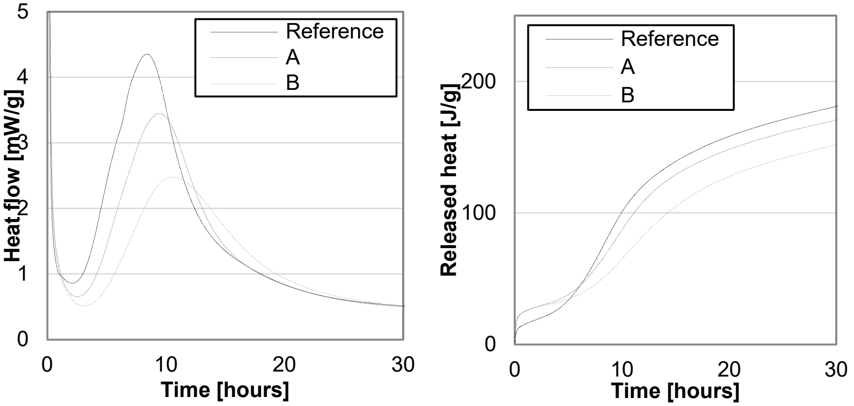


Figure 5.1: Flexural strength comparison of WWCBs manufactured with the Wood A and the Wood B

Since the WWCBs have been manufactured using the same recipe and therefore have a very similar moisture content, the difference in performance cannot be related to the different water availability for the binder reaction [187]. The density of boards made with Wood A is also slightly above WWCB made with Wood B, but this difference is minimal and cannot be explained by such significant differences between the two WWCBs.

5.3.2 Cement fibre interaction

Figures 5.2a and b depict the isothermal calorimetry measurements of the effect of the two types of spruce wood on the cement hydration. The heat flow and released heat are normalised to the mass of cement. The addition of Wood A to the cement paste slightly decreases the heat flow and slows down the cement hydration. However, as shown in Figure 5.2a, Wood B has a much more significant effect on the heat flow and the released heat (Figure 5.2b). The maximum peak of the cement hydration is slowed down by 1 h with the addition of Wood A and more than 2 h with Wood B. From Figure 5.2b, it can be seen a difference in total cumulative released heat during the exothermic reaction of cement while it is mixed with water/leachates. The difference between the reference sample and Wood A is minor.



a) **b)**

Figure 5.2: Effect of the Wood A and the Wood B on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

On the other hand, a significant difference is seen between the reference sample and Wood B. This phenomenon can be explained because the wood has extractives that can hinder or stop the cement hydration by interacting with the cement and the hydration products [11]. Based on Figures 5.2a and 5.2b, it can be assumed that Wood B contains more inhibitors than Wood A.

By using Pasca's equation (4.2) and isothermal calorimetry measurements (Figure 5.2a), the cement-fibre compatibility is calculated for these two samples. (Table 5.3). From these results, Wood A is compatible (85) whereas Wood B is moderately compatible (75) with cement which supports the observations shown in Figures 5.2a and b. However, this slight decrease in compatibility cannot be the only reason for the big difference seen with WWCB flexural strengths.

Table 5.3: Cement-fibre compatibility of white cement CEM I 52.5R and wood samples

Wood	Cement-fibre compatibility
A	85
B	75

5.3.3 Characterisation of wood fibres

The tensile strength of individual wood strands has been measured in order to evaluate if the quality of wood can be assessed from its smallest unit, which in the case of wood-wool cement board corresponds to one strand. The two types of wood have been tested, and the average results of tensile strength and E-modulus are shown in Table 5.4, and a characteristic stress/strain curve is also shown in Figure 5.3.

Table 5.4: Average value of the tensile modulus and the tensile strength of the tested wood strands

Wood	Modulus [N/tex]	Tensile strength [cN/tex]
A	1645 ± 349	1316 ± 437
B	1011 ± 363	512 ± 173

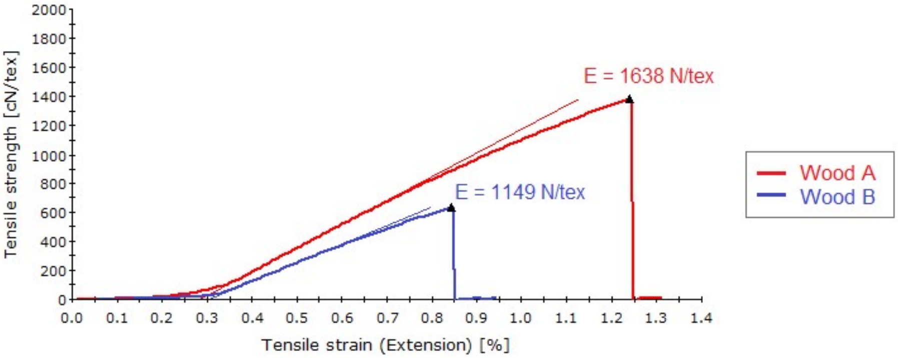


Figure 5.3: Characteristic stress/strain curve taken from an average strand for both kinds of wood. In red: Wood A; in blue: Wood B

Results show significant differences between the two types of wood. Wood A has a tensile strength two and a half times higher than Wood B (+ 157%). It has to be pointed out that the test's standard deviation is quite high, which is common with heterogeneous cellulosic fibres. Still, statistically, the lowest tensile strength value of Wood A is higher than the highest one of Wood B. The tensile moduli of the strands have also been studied. Similarly, Wood A shows greater values (+ 63%) than Wood B, even though in this case, considering the high standard deviation, this difference is not very significant.

This decrease in tensile strength means that the wood's microstructure was affected prior to wood strand production. Wood consists primarily of cellulose, hemicellulose and lignin (Table 5.5) [33]. In this study, it appears that the tensile moduli of the two types of wood (A and B) are sensibly the same. In composite materials, intrinsic properties such as the tensile modulus are defined by the rule of mixtures [199]. In lignocellulosic material such as wood, the intrinsic mechanical properties come from the cellulose fibrils located inside the hemicellulose and lignin matrix [200]. Therefore, this result indicates that cellulose has not been affected by internal degradation. Compared to the tensile modulus, the tensile strength of the fibres is defined by the cellulose fibrils and the rule of mixtures and by the quality of the interface and the load transfer assured by the matrix.

A probable hypothesis would be that the lignin or the hemicellulose have been slightly degraded during the wood storage. This degradation has a negligible effect on the bulk wood properties, but this effect is much more noticeable when cut into strands. In order to demonstrate this theory, microstructure analyses are done by SEM.

Figure 5.4 shows the micrographs of the surface and the transverse section of Wood A and B strands. The surface of Wood A strand is very similar to the available literature about spruce wood, where pits are easily observable and aligned along with the fibre (red box) [201]. The matrix is uniformly dispersed at the surface (red arrow), covering the whole surface and overlapping at the border of the pits (Figure 5.4a). However, as seen in Figure 5.4b, the surface of Wood B is different. The matrix seems less smooth, but more importantly, the pits are not well defined (blue box) and seem damaged (blue arrow). From the literature, this phenomenon looks like a brown-rot fungi bio-degradation, with fungal hyphae coming out of the pits [202]. However, in this case, the degradation seems even more pronounced. A close-up of the pit shows that the matrix is completely destroyed, and the fungi degradation is not clearly observable. The transverse section micrographs of Wood A and B are shown in Figures 5.4c and d, and both wood fibres have a very similar structure (red and blue arrows). Cell walls are well defined, and the only noticeable differences are mostly due to the sample preparation. As compared to some studies showing the transverse section of the different types of woods that have been degraded, the wood cells here, in both cases, seem to be intact with no visible shrinkage or distortion [203]. Moreover, no fungal hyphae are observable in both cases.

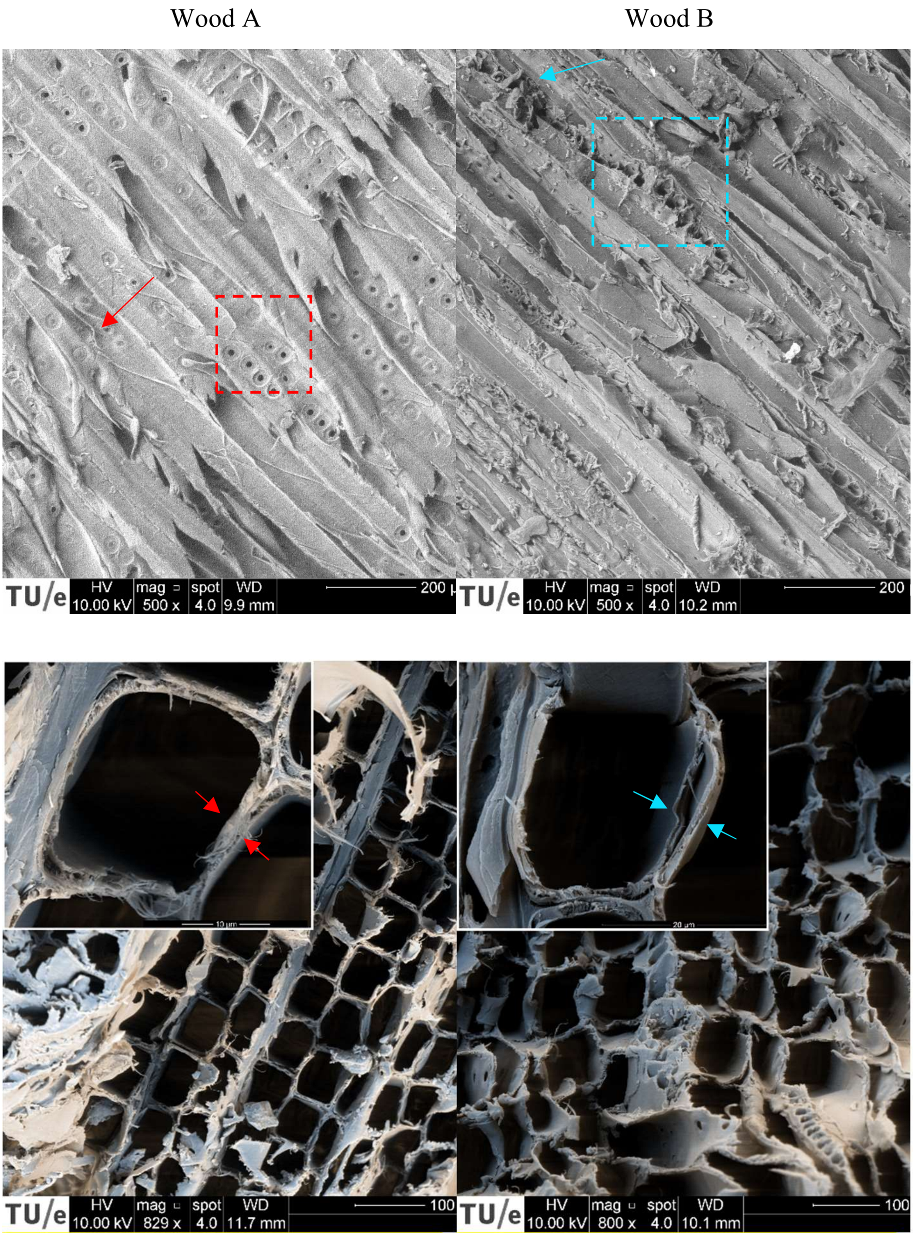


Figure 5.4: SEM micrographs of (a) Wood A strand surface; (b) Wood B strand surface; (c) transverse section of the wood A strand; (d) transverse section of the wood B strand

From these observations, several conclusions can be drawn. First, Wood A seems to be intact. There are no traces of any degradation, neither at the surface nor inside the cells and the micrographs are very similar to the conventional spruce characterised in the literature. On the other hand, Wood B has been locally degraded, close to the surface pits, and this degradation is quite important. Nevertheless, even though Wood B has been degraded, this phenomenon was not visible in the cross-section, where the cellulose fibrils are located. It would explain the mechanical behaviour of Wood B, with a strength decrease (i.e. local destruction of the hemicellulose/lignin matrix leading to an important stress concentration factor) but a relatively unchanged modulus (i.e. cellulose fibrils, with high tensile modulus, have not been damaged) as compared to Wood A.

5.3.4 Chemical characterisation of wood leachates

The leachates of the two wood types are analysed in order to evaluate the link between the organic inhibitors that can be contained in wood, the compatibility and low mechanical strength of the WWCB as characterised in the previous sections. Five monomeric sugars are measured, arabinose, galactose, glucose, xylose and mannose (Table 5.5), which are the main hydrolysis products of cellulose and hemicellulose [150]. Overall, Wood B has a much higher sugar content than Wood A. A correlation can be observed between the released heat during the first 30 h of cement hydration (Figure 5.2b) and the total amount of sugars (Table 5.5), where a high amount of sugars leads to a lower released heat.

Table 5.5: Comparison of Wood A and Wood B extractives measured by HPAEC after H_2SO_4 hydrolysis

Wood	**Arabinose** mcg/ml	**Galactose** mcg/ml	**Glucose** mcg/ml	**Xylose** mcg/ml	**Mannose** mcg/ml	**Total Sugars** mcg/ml
A	19.8	82.6	15.2	3.1	29.5	150.2
B	23.4	83.3	91.3	28.9	182.7	409.6

From the literature, it is known that the most problematic effect caused by monomeric sugars is mainly caused by glucose due to a disruption of C-S-H gel formations [21]. In this study, glucose is six times higher in Wood B than Wood A among the characterised polysaccharides. Nevertheless, any polysaccharides can cause nucleation poisoning of hydrate surfaces and thus can affect the retardation mechanism based on the absorption of the clinker gains [11]. For instance, xylose is also characterised to be problematic [17]. The amount of xylose is nine times higher in Wood B. Mannose is also leached out from Wood B. The literature shows that the hemicellulose may complex with metal ions in cement through mannose hydroxyls and then decrease crystallinity, hydration rate, and strength [17].

Alongside monomeric sugars, uronic acids are also known to have a retarder effect on cement hydration. In this study, two types of uronic acid are measured, namely galacturonic acid (GAA) and glucuronic acid (GLA). Both acids are derived from monomeric sugars, GAA is from galactose, and GLA is from glucose [162]. Table 5.6

depicts the concentration of GAA and GLA in the fibre leachates and shows the value of the pH of the leachates. As expected, the concentration of uronic acids is higher with Wood B. If monomeric sugars can cause a significant delay to the cement hydration due to their degradation products, the cement's pH during the hydration phase is also a critical factor. It may be affected by the numerous carboxylic acids leached by cellulosic fibres [16,17].

Table 5.6: Quantification of uronic acids measured by CG after methanolysis, as well as the pH value of the leachates

Wood	**Galacturonic acid** mcg/ml	**Glucuronic acid** mcg/ml	**pH**
A	4.4	17.9	5.9
B	27.9	24.5	5.4

Overall, results show Wood B is affected by the degradation of hemicellulose. Measurement of the leachates shows that the high concentration of polysaccharides (e.g. Glucose, mannose and xylose) and uronic acids in Wood B are direct results from the hydrolysis of the hemicellulose. However, this significant increase in polysaccharide concentration does not affect the wood/cement compatibility too much (CX' = 85 and 75 for Woods A and B, respectively). It can be explained by the confined degradation, which only happens close to the pits, limiting the diffusion of polysaccharides to the cement matrix.

5.4 Conclusion

This study aims to point out the difference between two very similar, commercially produced spruce wood-wool fibre batches. Results show that even though these two types of wood passed standard quality controls, they are significantly different in terms of compatibility, mechanical properties and microstructure. The following conclusions can be drawn:

- WWCBs are made with two types of wood. Wood A gives satisfactory results, far above the acceptable limit (i.e. 1.7 MPa), whereas the strength of Wood B is significantly lower and cannot fulfil the requirement. This major difference confirms the eminent difference between these two wood.
- Cement-fibre compatibility is calculated, and Wood B is slightly less compatible than Wood A, which is considered compatible (CX' = 85). In contrast, Wood B is considered moderately compatible (CX' = 75) with cement, which is one reason why Wood B resulted in low-quality WWCB.
- Mechanical characterisation of the strands shows that Wood B is clearly damaged as its strength is significantly lower than Wood A (- 63%). Microscopy shows evident damage close to the pit but not in the cell walls, explaining a possible matrix degradation (i.e. hemicellulose). On the other

hand, the cellulose seems untouched, as can be seen with the unchanged E-modulus between Wood A and B.

- Wood leachates are prepared from Wood A and B, and the polysaccharides and acid measurements confirm the previous observations. The degradation of hemicellulose causes an increasing amount of GAA, glucose, mannose and xylose in the fibre, and this degradation could be the result of fungi attack.

Overall, this study indicates that current quality control methods are not suitable for characterising micro degradation, which can have a significant effect on WWCB properties. From these results, cement/fibre compatibility and single-strand tensile tests are good degradation indicators. Thus, on an industrial scale, these methods could be used in the future in order to improve the existing quality controls of the wood prior to the manufacture of WWCB.

Chapter 6

6 Using alternative waste coir fibres as a reinforcement in cement-fibre composites

K. Kochova, F. Gauvin, K. Schollbach and H.J.H. Brouwers, "Using alternative waste coir fires as reinforcement in cement-fibre composites," . Constr. Build. Mater., vol. 231, 117121, 2019

6.1 Introduction

For decades, cement-wood composites have been used as a construction material [1]. Among the new generation of cement-wood composites are commonly used thanks to their good properties. Due to their high thermal insulating and sound absorbing properties with high porosity and low density (300-500 kg/m^3), the boards are mainly used as sound-absorbing ceilings, thermal insulation ceilings, and wall panels [2,3]. They can also be used indoor or outdoor as decoration or in permanent shuttering and roofing.

Wood fibres have many benefits like renewability, biodegradability, low cost and availability. Still, on the other hand, they also have some disadvantages: For instance, during the manufacturing process of WWCB (Figure 2.3), quality controls of the wood prior to cutting them to wood wool or after the processing show many problems related to the biodegradation of the wood. These degradations are caused by changes in the cell walls, which can significantly alter wood properties (e.g. strength, water absorption), and appearance. Moreover, the transportation of wood logs around Europe, which is the most energy-consuming operation in wood-wool processing, requires energy, which depends on the type of vehicle, the road and the weather conditions. For example, using a tractor and a truck to ship the wood trunks produces a volume of 0.94 to 8.53 kg m^{-3} of CO_2 emission per unit transported volume [167]. Moreover, growing just one selected type of wood leads to monocultures and the associated problems of low ecological diversity and the spread of diseases of pests [204]. To solve these issues, using natural waste fibres in order to substitute wood in composite materials is a good way to reduce primary materials and energy and reduce the cost of the raw materials and their processing.

Organic waste materials are known as lignocellulosic materials, and they can be obtained from wood or plants, as depicted in (Figure 2.5). Cellulosic fibres can be separated between waste fibres and plants, which are grown to be used as natural fibres for specific composite applications. natural waste fibres includes many different materials such as rice, wheat, barley, oat, coir, oil palm or bagasse fibres. Moreover, hemp or flax fibres can also be considered as a natural waste fibre in different countries when they grow these plants for yield and not for their fibres. Nowadays, in many countries, agricultural waste is becoming an environmental problem because these resources are growing fast and are eventually burned or buried, making the cost of natural waste fibres very low. Using natural waste fibres can be a way to recycle and reuse them in a more sustainable way. They are worldwide available, biodegradable, non-toxic, eco-friendly and could be a good candidate to replace the currently used fibres [5,105,205]. natural waste fibres are a good source of new types of materials in the production of cement-fibre composites due to the listed benefits. Short fibres can be used as a replacement for wood in dense boards, whereas long fibres could replace wood in lightweight boards and could also act as a reinforcement in lightweight concrete.

On the other hand, natural waste fibres also has some major disadvantages, which limit their potential applications. The main problem comes from the carbohydrates and water-soluble sugars in the fibres that can leach out and slow down or even stop the hydration of cement by forming a thin layer on the surface of cement grains and the nucleation poisoning of hydrate surfaces [11,14–18]. This problem can be solved by using pre-treatments or adding additives to cement composites [11,35,41].

Among the available candidates, one of the most promising waste fibre as a wood replacement in cement-fibre composites is the coir fibre extracted from the husk of coconut shell. The processing of coir fibres from coconut husks is simple and inexpensive. The first step consists of crushing the nuts and removing the white meat, then husks are dried for 7 – 10 days, and finally, the coir fibres are processed by a crushing machine extracting the fibres [80]. Those fibres have low cellulose and high lignin contents, which make these fibres strong and flexible. Due to its low density and high thermal conductivity, the coir fibres have a good predisposition for cement-coir composites' manufacture. [5,81]. Cement-coir composite made with coir fibre can have low density and would be inexpensive because most of the raw material needed to process it is coming from waste. According to Van Dam et al., in 2004, 40 million tons of coconuts yield more than 2 million tons of fibres. Still, only a small fraction of them are reused for composite material applications, although the chemical compatibility with cement has been proven to be unproblematic [117]. The total amount of soluble sugars in the fibre leads to the high compatibility level of coir fibre with cement. It is much lower than other natural waste fibres (e.g. bagasse, oil palm) [33]. Also, coir fibres' expected mechanical properties are reported to be higher than wood fibres, meaning that coir fibre boards would have better flexural strength than WWCB [5]. However, only a few studies focus on the utilization of coir fibres in composite materials and using this raw resource for the cement-fibre board would be a new way of valorising natural waste fibres. Because of the lack of literature about this topic, characterization of the material and optimization of the process is needed to create a composite that fulfils the existing standards.

This work aims to characterise the interface and interactions between cement and coir fibres to solve the potential problems in the cement-coir composites process. These new composites should at least match the physical and mechanical properties of conventional WWCB. It is known that coir fibre does not have a strong retardation effect of cement hydration. However, a pre-treatment with calcium hydroxide ($Ca(OH)_2$) is applied in order to modify the fibre's surface properties for better bonding between cement and fibre. Calcium hydroxide ($Ca(OH)_2$) is used in this study due to wide availability and more sustainability compared to the other pre-treatments and can extract polysaccharides. Due to the saturated solution, the liquid can be used several times. The strength of the coir fibres is analysed before and after this pre-treatment. Scanning Electron Microscopy (SEM) and pull-out tests are performed to characterize the bonding strength between cement and fibre. Finally, the mechanical properties of cement-coir boards are measured as well as their thermal properties.

6.2 Materials and methods

6.2.1 Materials

In this study, CEM I 52.5 R white is used as a binder and is provided by ENCI, the Netherlands. Its chemical composition is given in Table 6.1. Untreated and treated coir fibres are used with 40-50 cm length. The chemical composition and the monomeric sugars and uronic acids concentration of untreated coir and spruce fibres are given in Table 6.2 [33]. Spruce wood is provided by Knauf Insulation, the Netherlands and coir fibres are provided by Wageningen Food & Biobased Research, the Netherlands. Calcium hydroxide (min. 96% $Ca(OH)_2$) provided by Merck is used for the pre-treatment of coir.

Table 6.1: Chemical composition of ordinary Portland cement CEM I 52.5R white used in this study

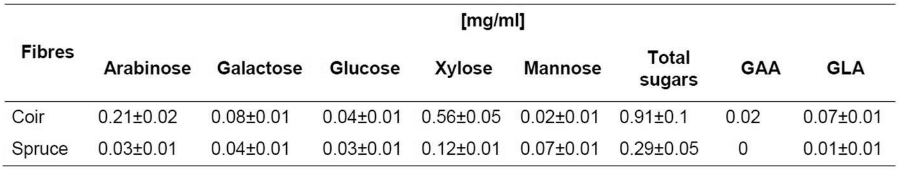
Chemical composition	[wt%]
CaO	62.21
SiO_2	20.93
Al_2O_3	3.90
Fe_2O_3	0.45
K_2O	0.12
Na_2O	0.11
SO_3	2.92
MgO	0.43
TiO_2	0.33
Mn_3O_4	0.02
P_2O_5	0.51

Table 6.2: a) Chemical composition of the natural fibres measured by HPAEC after H_2SO_4 hydrolysis; b) Monomeric sugars concentration in the leachates measured by HPAEC after H_2SO_4 hydrolysis and uronic acids concentration in the leachates measured by CG after methanolysis [33]

a)

		Fibres	
		Coir	**Spruce**
Cellulose		36.6	41.6
Hemicellulose		37.0	37.3
Lignin	[%]	22.2	19.4
Ash		1.9	0.4
Extractive		4.2	1.7

b)



Fibres	**[mg/ml]**							
	Arabinose	**Galactose**	**Glucose**	**Xylose**	**Mannose**	**Total sugars**	**GAA**	**GLA**
Coir	0.21±0.02	0.08±0.01	0.04±0.01	0.56±0.05	0.02±0.01	0.91±0.1	0.02	0.07±0.01
Spruce	0.03±0.01	0.04±0.01	0.03±0.01	0.12±0.01	0.07±0.01	0.29±0.05	0	0.01±0.01

6.2.2 Methods

6.2.2.1 Pre-treatment

A saturated solution of $Ca(OH)_2$ is used for pre-treatment of coir with a pH close to 12. Untreated fibres are soaked in the solution for 24 h at 20°C. After pre-treatment, two conditions are studied:

Firstly, the coir fibres are removed from the solution and put in an oven. Those pre-treated fibres are called non-washed fibres.

Secondly, the coir fibres are removed from the solution, washed once with tap water and then put in the oven. Those fibres are called washed fibres, and both treated fibres are dried at 60°C.

6.2.2.2 Boards processing of the cement-coir composites

Based on a calculation of the surface area of the coir fibre, the optimal fibre/cement (f/c) and water/cement (w/c) ratios are applied in the mixture design. Three different ratios for w/c (0.7, 0.8, and 0.9) and f/c (0.53, 0.62, and 0.75) are chosen in order to evaluate the optimum condition to maximize the mechanical, physical and thermal properties of cement-coir composites. The fibres are mixed with cement paste, placed into a mould (dimension: 15x30 cm), and then pressed for 24 h. The composite is then cured in plastic sheets for seven days and dried for three days at room temperature. Composites are dried in the oven for 2h at 50°C prior to analyses. This procedure is similar to the production of commercial WWCB.

6.2.2.3 Fibre characterization

A Phenom Pro X Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) are used to analyse the surface of untreated, treated fibres as well as fibres covered with cement. Micrographs are recorded by using a backscattering electron detector at 15 kV, and spots of treated fibres were measured three times.

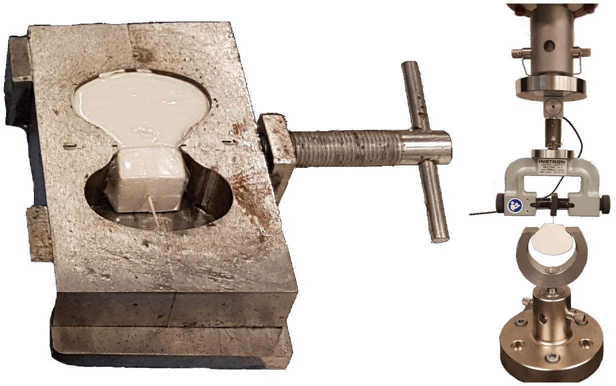
Samples of untreated and treated dried and milled coir fibres were tested by two different methods. X-Ray Diffraction analysis is performed using a D2 (Bruker) with a Co anode and a Lynx eye detector in order to analyse structural changes between untreated and treated fibres. Fourier Transform Infrared Spectroscopy (FT-IR) spectra are recorded using a Perkin Elmer Frontier FT-IR with a GladiATR diffuse reflectance device in order to characterize the effect of the pre-treatment at the fibres' surface. Eight scans are acquired with optical retardation of 0.25 cm and a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}.

6.2.2.4 Tensile properties of fibres

The tensile strength of fibres is measured using an INSTRON 5967 machine with a 100N load cell. The measurements are conducted with a crosshead speed of 5 mm/min. Untreated and treated fibres are mounted between the grips where each of the upper and lower jaws covers 2 cm of the sample. The distance between the jaws (l_o) is set at 100 mm. More than 15 specimens are tested, and the average strength of the fibres is determined. The tensile test is measured as a function of the fibre's linear density (tex) by measuring its length and weight.

6.2.2.5 Pull-out test

The pull-out test is conducted to determine if the fibres in the cement matrix pull out or break when the load is applied to the reinforced cement samples. The value, which is obtained from this test, is tensile strength (cN/tex). Eight fibres of three bunch of fibres (untreated, treated with washing and treated without washing) are embedded in the mould at a spacing of 3 cm on each side and filled by cement (Figure 3a). The length of fibres inside the cement matrix is set at 3 cm, which corresponds to 50% of the total fibre length. The moulds are covered with plastic foil for 24 h and tested after seven days. An INSTRON 5967 machine equipped with a 100 N load cell is used to test the bonding strength of the samples (Figure 6.3b). The test specimen is placed to the bottom, and the free end of the fibre is held by the upper grip. The fibre-held jaw is moved upward at a rate of 5 mm/min until failure.



a) **b)**

Figure 6.3: a) Pull-out mould; b) Test set-up designed for pull-out testing

6.2.2.6 Flexural strength of the composites

The bending strength of composites is measured at ten days by a three-point flexural test on samples with dimensions of 5 x 20 x 1.5 cm by using an INSTRON 5967 bench. The testing speed is set at 1.5 mm/min with a support span of 15 cm. four samples of each w/b and c/f ratio and untreated, treated, non-washed, and washed are tested. As a reference, WWCB with a maximum thickness of 15 mm should have a minimum bending strength of 1.7 MPa according to the BS EN 12089, *Thermal insulating products for building applications* standard [197].

6.2.2.7 The thermal conductivity of composites

Thermal conductivity is measured on cement-fibre composites with a thickness of 15 mm by a heat transfer analyser ISOMET 2104. As a reference, WWCB with a thickness between 15 and 30 mm have a thermal conductivity range of 0.08 – 0.11 $W.m^{-1}.K^{-1}$ according to the BS EN 12089, *Thermal insulating products for building applications* standard [197].

6.3 Results and discussion

6.3.1 Characterization of fibres before and after pre-treatment

6.3.1.1 Chemical characterization of coir fibres

FT-IR spectroscopy can be used as a semi-quantitative analysis for cellulosic fibres [206]. In this study, the influence of the pre-treatment on the fibre surface is studied by comparing FT-IR spectra of untreated and treated fibres. The main known problem from the literature is hemicellulose, which has an effect on cement hydration. Moreover, wax and others impurities on the surface can also affect the cement/fibre interaction [33].

Figure 6.4 summarises the effect of the pre-treatment on the coir fibres observed by FT-IR. Table 6.3 summarizes the major peaks characterized in the FT-IR spectra. The FT-IR spectra of untreated and treated coir fibres are mostly similar. The main differences are seen with the peaks at 2980-2800cm-1, corresponding to wax on the fibres' surface and with the peak at 1750-1730 cm^{-1}, corresponding to the hemicellulose. Peaks at 1150-1400 cm^{-1}, corresponding to pectin, lignin and hemicellulose, also almost disappear after pre-treatment. $Ca(OH)_2$ is not observed in these spectra since its characteristic peaks are known to be at 2507, 1795, 1423 and 871 cm^{-1} and are not visible in Figure 4. [207].

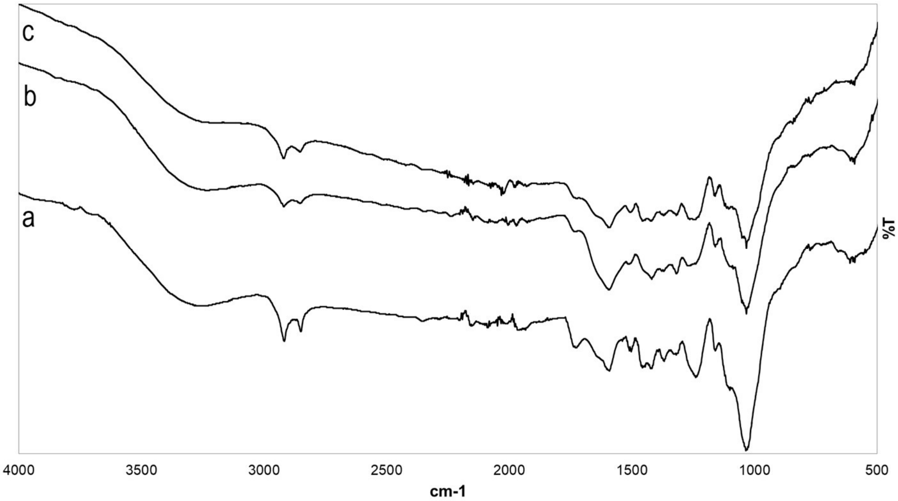


Figure 6.4: FT-IR spectra 4000 – 500 cm^{-1} of coir fibres: a) Untreated fibre; b) treated, non-washed fibre; c) treated, washed fibre

Table 6.3: Infrared absorption frequencies of untreated and treated coir fibres [8,42,177,206]

Wavenumber [cm-1]	**Vibration**	**Source**
3300	O-H linked shearing	Polysaccharides
2980-2800	CH_2 symmetrical stretching	Wax
1650-1630	OH	Water
1750-1730	C=O stretching	Hemicellulose
1595	Aromatic ring vibration + C=O stretching	Lignin
1505	C=C aromatic symmetrical stretching	Lignin
1465	C-H deformation	Lignin
1425	CH_2 symmetric bending, C=C stretching in aromatic groups	Pectin, lignin, hemicellulose
1370	CH bending	Polysaccharides
1320	C-O aromatic ring	Cellulose
1240	C-O aril group	Lignin
1160	C-O-C asymmetrical stretching	Cellulose, hemicellulose
1035	C-O, C=C, C-O-C stretching	Cellulose, hemicellulose, lignin

The XRD measurements of untreated and treated coir fibres are presented in Figure 6.5. [155,208,209]. The untreated coir fibre shows the bread peaks of crystalline cellulose together with traces of quartz. The peak at 30.32 °2Theta could not be identified. The amorphous content of the fibres decreases after the pre-treatment, as can be seen by the lower background. This phenom is due mainly to removing hemicellulose and other amorphous constituents, while the cellulose remains largely unaffected. No remaining $Ca(OH)_2$ or $CaCO_3$ from the pre-treatment can be detected in the fibres.

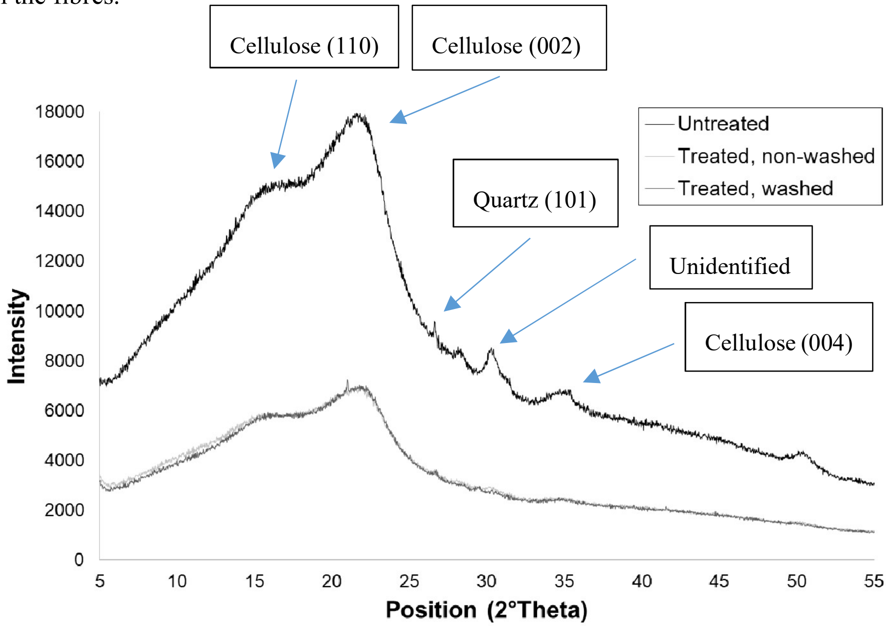
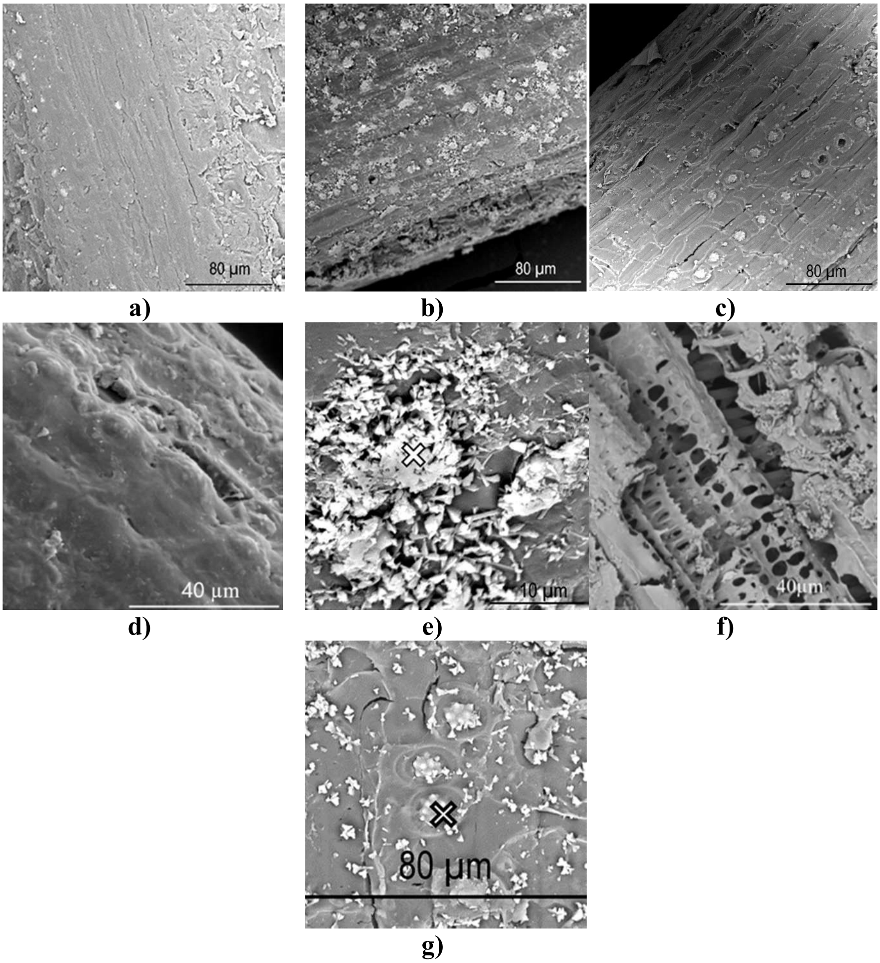


Figure 6.5: XRD analysis of untreated and treated coir fibres

When an alkali treatment is applied, it has an impact on the morphology, molecular and supramolecular properties of cellulose. Consequently, fibres are stiffer, accessible, and have changes in crystallinity and pore structure [208].

6.3.1.2 Surface characterization of fibres

Surface characterization of the fibres is accomplished in order to evaluate the effect of the pre-treatment on the morphology of the coir fibre. Figures 6.6a – g shows the surface morphology of untreated and treated coir fibres by SEM.



a) b) c)

d) e) f)

g)

Figure 6.6: SEM: a) Untreated coir fibre 80 µm; b) Treated, non-washed coir fibre 80 µm; c) Treated, washed coir fibre 80 µm; d) Detail on untreated coir fibre 40 µm; e)Detail on treated, non-washed coir fibre 40 µm; f) Treated, washed coir fibre 10 µm, measured spot by; g) Treated, washed coir fibre 80 µm, measured spot by EDX

The pre-treatment led to morphological changes due to the removal of compounds like wax and hemicellulose. From the literature, it appears that a thick layer covers the fibre surface (Figures 6.6a and b) can be characterized as wax and oil [35,86,178]. Figure 6c shows the treated, non-washed coir fibre, where the wax is entirely removed, but a residue is still visible around the pits. EDX analyses are performed at the surface of the fibre (Table 6.4a) in order to characterize the composition of these residues, and it appears that these compounds are calcium-based (Figure 6.6d) coming from the $Ca(OH)_2$ that crystallised on the fibre surface pores when the saturated solution dries. On the other hand, in Figure 6.6e, no calcium residues are visible, showing that the washing step realized after the pre-treatment helps remove the remaining $Ca(OH)_2$. However, traces of unknown micrometric particles inside the pores can also be seen. By doing an EDX characterisation (Table 6.4b), it is discovered that the particles are silica-bodies (Figure 6.6g) which tend to be concentrated in pores [179]. This process is not unusual because coir fibres naturally absorb inorganic compounds as a biological process [181]. It is noticeable that a long pre-treatment (24 h) with washing can be harmful to some fibres, as seen in Figure 6.6f, where the fibre is clearly damaged. However, the same pre-treatment (Figure 6.6e) also shows a clean surface without more extensive damage.

Table 6.4: Semi-quantitative EDX characterization: a) Treated, non-washed coir fibre; b) Treated, washed coir fibre

	Element Name	**Atomic Conc.**
a)	Calcium oxide	7.1±4.4
b)	Silicon oxide	13.2±5.2
	Calcium oxide	1.2±1.2

Overall, pre-treatments can remove some constituents of the coir fibre that appears to be wax, oil and hemicellulose. Moreover, the morphology of the fibres changes as pre-treatments roughens their surface. Furthermore, they also almost removed all silica-bases and calcium residues, which eventually may improve the cement/fibre interaction.

6.3.1.3 Mechanical properties of fibres

The tensile strength of untreated and treated fibres are shown in Figure 6.7. The average stress/strain curves of each sample are shown in Figure 6.8. The tensile strength of the untreated fibres is compared with the tensile strength of treated fibres with two different conditions, namely non-washed and washed, in order to evaluate the efficiency of rinsing the remaining residual $Ca(OH)_2$ that could stay on the fibre. It must be noticed that the standard deviation of these tests is very high (34 – 45%), which is quite common with heterogeneous cellulosic fibres. Student's t-test: A comparison of two means is added to show differences between untreated and treated fibres due to the high standard deviation. The results can be seen in Table 6.5.

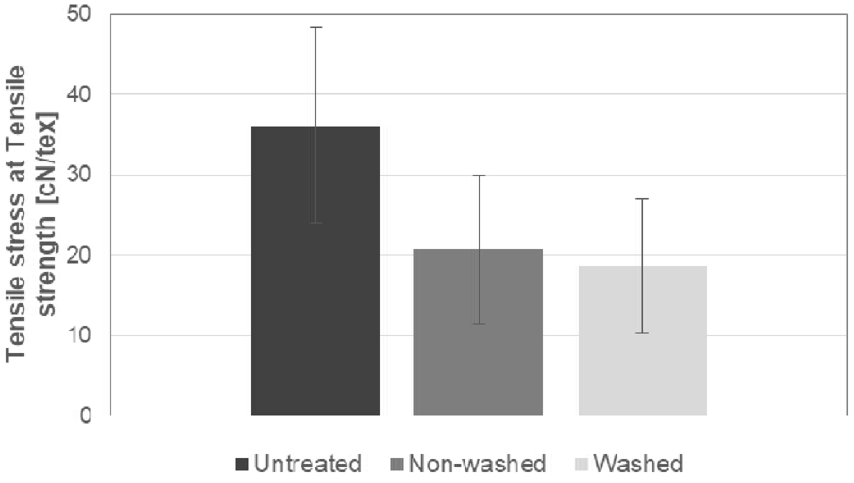


Figure 6.7: Tensile strength of untreated and treated coir fibres

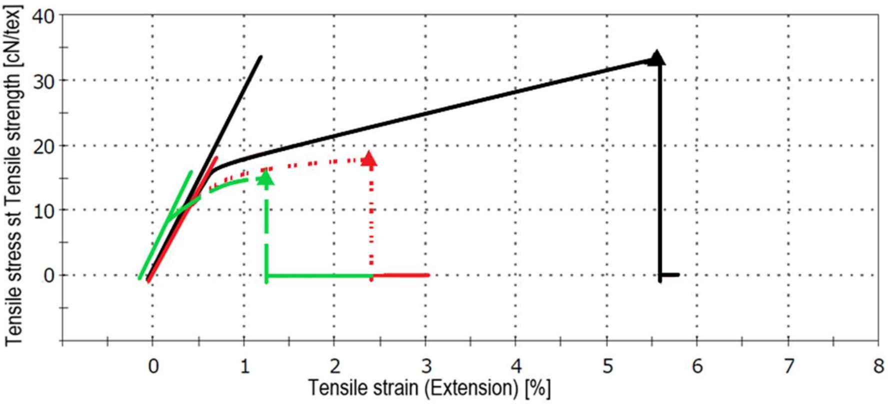


Figure 6.8: Characteristic tensile stress at tensile strength curves. In the solid black line: untreated fibre, long dash green line: treated, non-washed fibre, doth red line: treated, washed fibre

Table 6.5: Student's t-test: Comparison of two means

Fibres	Number of tests	Mean	SD
Results for Untreated fibres	21	35.1	11.6
Results for Non-washed fibres	24	19.6	7.5
Results for Washed fibres	23	19.0	8.4

t-test report for Untreated and Non-washed fibres

t-experimental = 5.371
P (type 1 error) < 0.0001
Therefore:
The means ARE different at CL 90%
The means ARE different at CL 95%
The means ARE different at CL 99%

t-test report for Untreated and Washed fibres

t-experimental = 5.307
P (type 1 error) < 0.0001
Therefore:
The means ARE different at CL 90%
The means ARE different at CL 95%
The means ARE different at CL 99%

t-test report for Non-washed and Washed fibres

t-experimental = 0.2886
P (type 1 error) = 0.7742
Therefore:
The means ARE NOT different at CL 90%
The means ARE NOT different at CL 95%
The means ARE NOT different at CL 99%

Figure 6.7 shows a substantial reduction in tensile strength of treated fibres (43 and 49%), meaning that the pre-treatment causes a decomposition of the fibres, which significantly affects the fibre’s tensile strength. The maximum reduction is observed when the fibre is washed, with a tensile strength decrease of 49%, which was slightly higher than non-washed fibres (- 43%). Statistically, even the lowest tensile strength value of the untreated coir fibres is higher than the average tensile strength of treated fibres. The significantly lower strength can be characterised by the chemical dissolution of lignin in the alkaline environment. Another explanation may be an absorption of the alkaline solution into pores making the fibres more brittle, as can be seen in Figure 6.8 [100].

The physical and mechanical properties of natural fibres are defined by their chemical composition (i.e. cellulose, hemicellulose and lignin) as well as the organization of the cell walls that can be measured with a cell wall/lumen ratio [210]. The strongest and stiffest component in natural fibres is cellulose. In contrast, hemicellulose does not have a significant effect on cellulose due to its solubility in water and high water absorption. The lignin is mainly a bonding agent, acting as the matrix in this cellulosic composite [211]. As characterized by FT-IR and SEM, pre-treatment does change the hemicellulose content, as well as the surface of the fibres. The wax is also removed, leading to rougher surfaces. Because of these reasons, treated fibres have significant lower tensile strength than untreated fibres.

From their results, it can be concluded that the fibre's strength is significantly lower after pre-treatment, which could influence the final composite. On the other hand, the hypothesis in this study is to significantly change the fibre microstructure in order to achieve better bonding between cement and fibres, meaning that this drop in mechanical properties is necessary in order to improve the composite strength.

6.3.2 Bonding between cement and coir fibres

6.3.2.1 Single fibre pull-out test

The pull-out test determines the bonding strength between cement and different coir fibres. The tensile stress at the cement-fibre bond strength is calculated by dividing the maximum pull-out load by the surface area of the fibre. The average and characteristic pull-out curves for each condition are shown in Figure 6.9. The average results for untreated and treated coir fibres in the cement matrix are demonstrated in Table 6.6. The highest pull-out strength has been measured for treated and non-washed coir fibres. As compared to other fibres, the reduction is about 2% for untreated coir fibres and 11% for treated, washed fibres. As seen in previous tensile testing of fibres, the standard deviation with natural fibres is very high, with more than 30% deviation. During pull-out tests, a few untreated and treated, washed fibres are broken, where the tensile strength of those broken fibres was lower than the tensile strength of the single fibre in the previous test of single fibres. The reason can be explained by the variation of the cross-section dimensions of these fibres.

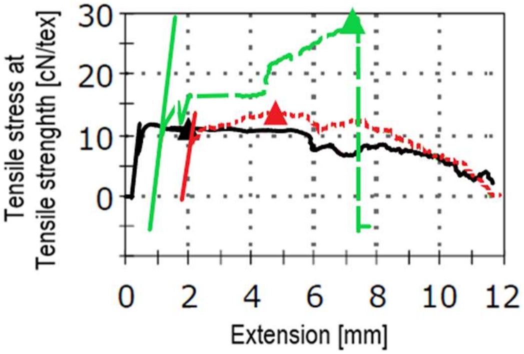


Figure 6.9: Characteristic tensile stress at tensile strength curves of the pull-out test. In the solid black line: untreated fibre, long dash green line: treated, non-washed fibre, doth red line: treated, washed fibre

Table 6.6: The pull-out test of untreated and treated coir fibres

Pre-treatment	Tensile stress at Tensile strength [cN/tex]
Untreated	13.8±4.2
Treated, non-washed	14.1±6.3
Treated, washed	12.6±3.4

Nevertheless, the pull-out strength of untreated and treated coir fibres cannot give additional information to assess the interface. In order to study the correct behaviour at the interface, stress/strain curves must be analysed, as shown in the literature by Beltran and Schlangen [212] and Rathod [213]: During the pull-out test, fibre can have four different behaviours, namely constant friction, slip softening, slip hardening or fibre failure, as it can be characterized in Figure 6.10.

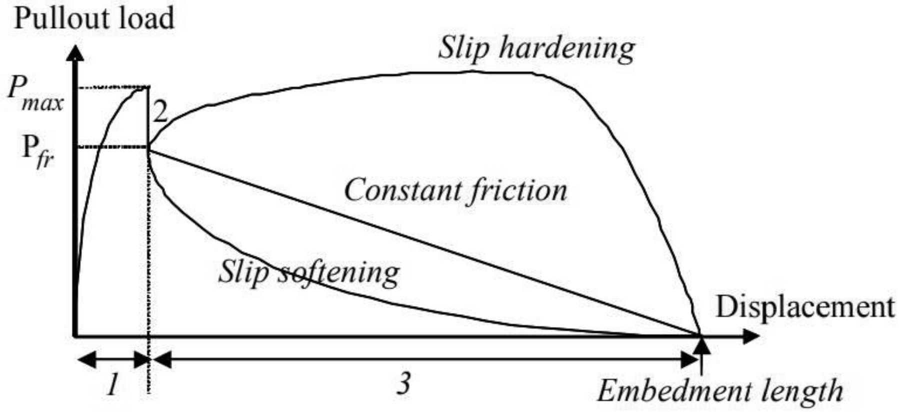


Figure 6.10 Schematic description of the four different fibre pull-out behaviour, as shown by Beltran and Schlangen [212]

Following this hypothesis, each sample is characterised by untreated and treated fibres' behaviour and summarized in Figure 6.11.

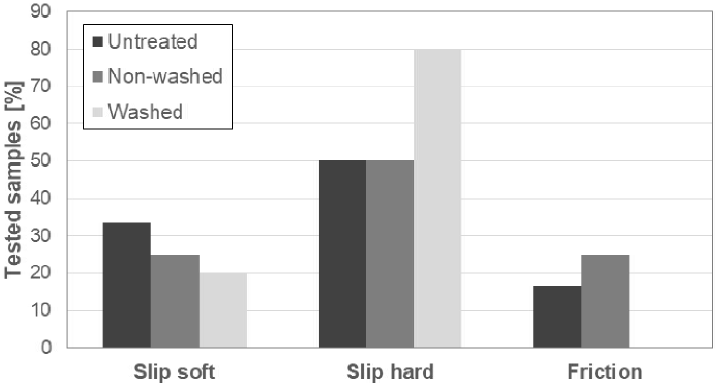


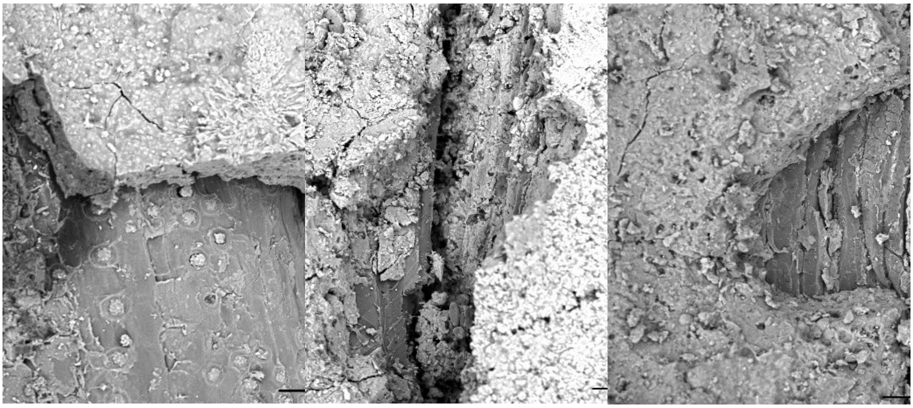
Figure 6.11: The pull-out test behaviour of untreated and treated coir fibres

All samples undergo mostly a slip hardening behaviour for more than 50% of the time, which means that when the fibre is pulled out, an increasing load resisting the fibre debonding occurs. However, the treated and washed coir fibres show no friction during the pull-out test, and almost all tested fibres have a slip hardening behaviour (more than 80% of the washed and treated fibres). Untreated fibres undergo a slip softening behaviour 33% of the time, identifying the bad interface between these fibres and the matrix. It shows that no additional load is applied when the fibres are pulled out, meaning that the debonding is easier.

Overall, the treated and washed coir fibre has a better bonding strength among all conditions. It can be explained mainly by the unwanted substances removed from the surface (i.e. wax, oil, silica bases), helping the cement hydration occur inside the pores, increasing the interface strength between the fibre and the matrix.

6.3.2.2 Fractography

Figures 6.12a - c show SEM micrographs of coir fibre embedded in the cement matrix. The fibres are removed from cement-coir composite after tensile testing prior to SEM characterization.



a) **b)** **c)**

Figure 6.12: SEM of bonding between cement and coir fibres: a) Untreated coir fibre; b) Treated, non-washed coir fibre; b) Treated, washed coir fibre

In Figure 6.12a, a visible gap between the untreated coir fibre and the surrounding cement matrix can be seen, showing the poor fibre/matrix interfacial adhesion. On the other hand, treated fibres (Figures 6.12b and c) show that the fibre/matrix interfacial gaps are significantly reduced in both cases, showing a better interfacial bonding. It is demonstrated that the pre-treatment affects the interface between the cement and fibre, mostly because of the impurity's removed from the surface. Moreover, the calcium residue, which remains on the surface, could help to form better bonding between the fibre and the cement coating. From these results, the best fibre/matrix interfacial adhesion was characterized with treated and washed fibre (Figure 6.12c), where the impurities such as silica-based particles or unwanted constituents of the fibre are removed from the surface, allowing the cement matrix to penetrate into the pores and crystallised inside the fibre, confirming the observations made after the pull-out tests.

6.3.3 Mechanical and physical properties of the composites

6.3.3.1 Mechanical performance of the composites

Figure 6.13 shows manufactured cement-coir composites, which are cut and used for testing the properties of the composites. The cement-coir composites mechanical performances are depicted in Figure 6.14, showing the flexural strength as a function of the density of manufactured cement-coir composites.

Figure 6.13: The cement-coir composites made for the different conditions

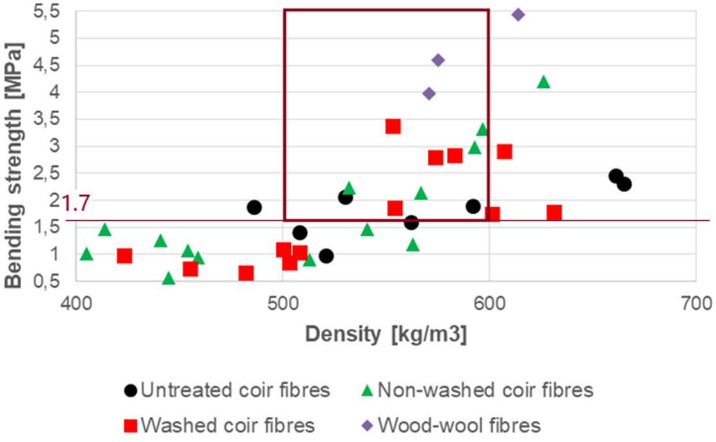


Figure 6.14: Bending strength/ density of cement-coir composites

As described in the BS EN 12089 standard [197], the acceptable bending strength for WWCB is 1.7 MPa. The graph (Figure 6.14) shows that the bonding strength is highly dependent on the density, and some cement-coir, depending on their composition, can be above the limit or way below. These results can be divided into three different density ranges. The first density range (400 – 500 kg/m^3) shows very low bending strengths with all treated samples, caused by the low cement content. These samples are manufactured with a low fibre to cement ratio (f/c = 0.53) and a high-water content (w/c = 0.9). The second density range is around 600 - 700 kg/m^{3,} and all the samples are above the strength limit. However, the standard also requires a density below 600 kg/m^3 due to the potential applications (e.g. ceiling) of these materials. The material's weight is explained by a manufacturing process that is not optimal, where an excess of cement is used. In both situations (i.e. the different density ranges), problems come from the cement and fibre distribution in the composites.

The last density range is 500 – 600 kg/m^3, which is ideal for the composites, as described in the standard. The composites with untreated coir fibres are mostly below the limit and range from 1 to 2.1 MPa. This result confirms the necessity of a fibre treatment for the manufacture of coir/cement composites. When treated, fibres have a better bonding with the cement, as seen with fractography or pull-out tests. However, the difference between non-washed and washed coir fibres is minor in composites, samples without washing range from 0.9 to 3.3 MPa and with washing from 0.8 to 3.4 MPa. It appears that the decrease of the tensile strength of the fibre does not affect these results significantly or are counterbalanced mainly by the beneficial effect of the higher roughness of treated fibres and the removal of unwanted constituent at the fibre surface. In comparison, wood-wool cement boards were made with the same method as cement-coir composites for control and added to Figure 6.14.

Overall, the treated fibres provide good results as compared to untreated fibres. However, it could be improved since some samples are still slightly below the strength limit. From Figure 13, it is evident that the distribution of fibres in the composites should be better, which can be obtained using a different and more consistent processing method. In this study, a wet method is used (i.e. first the cement is mixed with water and then fibres are added), and a dry method (i.e. the water is mixed with fibres and cement is added) can minimalize the clustering of fibres.

6.3.3.2 Physical properties of the composites

As a function of composite density for all the composites, thermal conductivity is displayed in Figure 6.15. These results indicate a dependence on thermal conductivity and density.

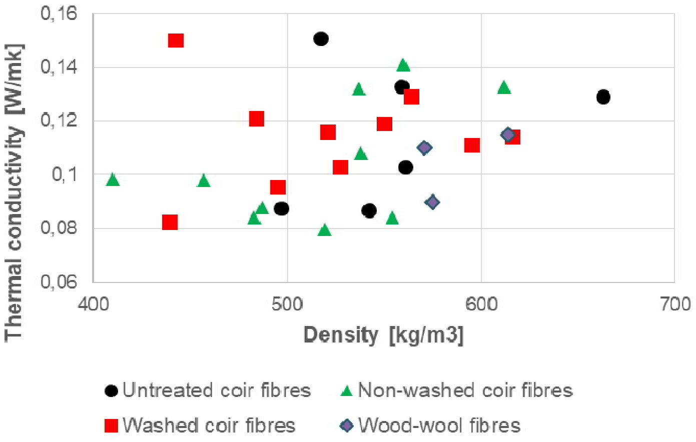


Figure 6.15: Thermal conductivity of cement-coir composite as a function of board density

As seen in the previous section, the density of the acceptable cement-coir composites ranges between 500 – 600 kg/m^3. Subsequently, with the composite properties, the thermal conductivity is the following: 0.126 W/m.K for the untreated fibres, 0.109

W/m.K for the treated, non-washed fibres and 0.116 W/m.K for the treated, washed fibres. WWCB is used in various industrial and residential applications where good thermal properties are necessary. The range for thermal conductivity standard of WWCB is between 0.08 – 0.11 W/m.K, meaning that the thermal conductivity of WWCB and the cement-coir composites are in the same range. However, composites made of untreated fibres are slightly off-limit, showing once again the necessity and the benefit of using treated fibres.

6.4 Conclusion

This study shows that composites made of coir fibres, an natural waste material, have adequate thermal and mechanical properties and can be used in the building industry for diverse applications. Moreover, the following conclusions can be drawn:

- Pre-treatments cause significant physical and mechanical changes to the coir fibres. It appears that the hemicellulose is removed from the surface of the fibre, as well as wax, oil and silica-based compounds. Due to those changes, treated fibres' tensile strength significantly decreases (- 46% on average).
- Morphological analyses done by SEM show that the fibres roughness significantly changes with pre-treatment. Moreover, calcium residues are visible after the pre-treatment and can explain the influence of a washing step after the pre-treatment.
- Pull out tests are performed in order to characterize the cement/fibre interaction. It appears that pre-treated fibres have a better interface with the cement than untreated fibre, with less slip softening and more slip hardening behaviour during the tests. Washed fibres also have a better interface than unwashed fibres because of the removal of unwanted constituents.
- The thermal and mechanical properties of the cement-coir composites are very close to conventional WWCB. The standard limit for bending strength (1.7 MPa), in the acceptable density range (500 – 600 kg/m^3), is achieved with treated fibres with both conditions: non-washed and washed. The thermal conductivity is in the range of 0.08 – 0.11 W/m.K. The benefit of pre-treatment is thus proven since the overall properties of the boards are improved.

Chapter 7

7 Water hyacinth as an alternative natural fibre in cement composites

K. Kochova, F. Gauvin, K. Schollbach and H.J.H. Brouwers, "Water hyacinth as an alternative organic fibre in cement composites,". Submitted..

7.1 Introduction

Cellulose fibres are very versatile, and they can be used as a filler or a reinforcement in cement composites or lightweight aggregate concrete. They can have various physical and mechanical properties (such as conductivity, density, porosity, rigidity, resistance, thickness, etc.) based on their origin and differences in their tissues which corresponds to their anatomy [195]. The use of cellulosic materials (alternative raw materials, waste, and wood) has accelerated rapidly over the past decade [5]. Many cement-based products using cellulose exist, such as cement-bonded composite, lightweight concrete, wood wool cement boards and many more [4–6,50]. Several examples of usage of natural fibres in the construction industry are displayed in Table 7.1.

There are various ways to bind fibres, which depends on the application of the end product. Cementitious materials (i.e. ordinary Portland cement (OPC), gypsum and magnesite) or polymers (i.e. PET, PP, PVA) are used as a bonding agent to manufacture fibre boards [5,9,115–124,35,125–129,36,53,67,73,78,113,114]. In a few cases, only heat is applied to create a binderless board [117]. It is also possible to produce concrete with natural fibres as lightweight aggregates for example) [51,114,214].

Table 7.1: Usage of different natural fibres [5,9,115–124,35,125–129,36,53,67,73,78,113,114]

Fibre	**Application of natural fibres**
Bagasse	Cement fibres composites, particleboard with urea-formaldehyde, particleboard
Coir	Cement coir board, cement bonded composite, particle board-coir, durian peel, urea-formaldehyde, binderless board, coir/epoxy composites and coir/PP composites
Cornstalk	Fibre cement composites with pulp corn stalk, medium density fibreboard with urea-formaldehyde
Hemp	Concrete, cement/fibre, polypropylene fibres composites, hemp fibres/PP composites and hemp fibres/epoxy composites
Oil palm	Cement bonded board, cement bonded board, fruit bunch fibres/PP composites, oil palm/phenol formaldehyde composites, oil palm/polyester resin composites and PVC composites
Reed	Composites with maleic anhydride functionalised polypropylene, virgin propylene and $CaCO_3$, UF-bonded board
Rice straw	Binderless board, cement bonded board
Water hyacinth	Polyester w. hyacinths composites, w. hyacinth fibres-polyester composites
Wheat straw	Particleboard with urea-formaldehyde, particleboard with wood and urea-formaldehyde, particleboard with urea-formaldehyde and PVA, cement bonded board, UF-bonded board
Wood	Wood wool cement board, cement bonded board

As it can be seen in Table 7.1, each fibre has its own usage in the building sector. Most fibres are used for the production of fibreboards. The use of alternative waste fibres is especially interesting to reduce the substantial environmental global impact of the building industry [5,6,146]. There are waste resources that can be used to develop sustainable construction materials [7]. Water hyacinth (WH) is one such fibre and can be used as a building material in several forms (cement-bonded boards, lightweight concrete or even as binderless particleboard) as well.

WH is an invasive species from the Amazonas that causes severe environmental problems in China, East Africa and other areas [82–84]. The plant overgrows and covers water surfaces, reducing sunlight penetration and lowering oxygen content in water, affecting water ecosystems. Ships also have a problem travelling, and many canals can become clogged, leading to problems with irrigation and drainage [82,83]. The plants can double in size in a few days under conditions such as high temperature and humidity. The plants form cohesive floating mats and can cover large water surface areas. They can be spread by winds and regenerate from fragments of stems that can remain viable for more than six years [83]. In order to keep the spread in check and protect bodies of water, the WH is often removed, which makes it available in large quantities. WH consists of 45% leaves, 26% petiole and 29% roots and has a moisture content of around 92% with a pH of around 7.3 [84]. However, a proper understanding of the anatomy, chemical composition, and structure of WH is missing in the literature. Most of the literature focuses on using WH for biofuel (i.e. bioethanol and biogas) for several reasons, such as naturally grown vegetation, easily degradable, resistance to pests, insect and diseases and high hemicellulose and low lignin content per dry fibres [97]. However, water hyacinth could also be used in cement composites and replace wood or serve as a lightweight aggregate. Its porous structure could give good composite acoustic and thermal properties [50]. However, due to its very porous structure and, therefore, high water absorption, using those fibres is challenging [85]. Moreover, another problem of WH use in cementitious materials is its negative effect on cement hydration [33].

Preliminary research on untreated WH as a possible aggregate for lightweight concrete shows that pre-treatment is necessary to remove inhibitory carbohydrates and water-soluble sugars [11,14–18,215]. Their effect on cement hydration can be described as a mechanism based on the adsorption of extractives on the cement grains and the nucleation poisoning of hydrate surfaces [11] and is described in more detail in Chapter 2. Another problem with WH is its porous structure and, therefore, very high-water absorption, leading to disruption on cement hydration. These problems can be solved using fibre pre-treatments. One of the most effective ways is alkaline treatment at higher temperatures and concentrations due to many advantages, such as breaking hemicellulose oligomers and increasing the hydrophilicity of natural fibres, dissolving lignin by hydrolysing acetic acids and esters. It also does not produce by-products like acid pre-treatment does, which can influence the cement hydration [10,131,132]. A good and environmentally friendly alternative to sodium hydroxide (NaOH) is calcium hydroxide ($Ca(OH)_2$) due to its wide availability and suitability in comparison with other pre-treatments [32,43,44].

This research aims to investigate the use of water hyacinth in cementitious building materials. The influence of chemical pre-treatment on the fibres structure was studied as well as the impact of treated WH fibres on the cement hydration as a potential option for increasing cement/fibre compatibility and avoiding problems further investigating lightweight concrete. Water absorption was measured for 24 and 48 h. FT-IR and SEM are applied to characterise structural and chemical differences between untreated and treated fibres. The influence of fibres on the cement hydration is evaluated using an isothermal calorimeter, and cement/fibre compatibility is calculated from those results. This study aims to develop a deeper understanding of WH, its characteristics and investigate a comparison between untreated and treated fibres, explain differences between them and show possibilities to use WH as a new material in cementitious materials and lightweight concrete.

7.2 Materials and methods

7.2.1 Materials

Water hyacinth (WH) used in this study is provided by Wageningen Food & Biobased Research, the Netherlands (Figure 7.1). The chemical composition of water hyacinth is given in Table 7.2 [33]. For the alkaline treatments, calcium hydroxide (min. 96% $Ca(OH)_2$) from Merck is used. Ordinary Portland cement CEM I 52.5 R (OPC) from ENCI, the Netherlands, is used as a binder, and its chemical composition is given in Table 7.3.

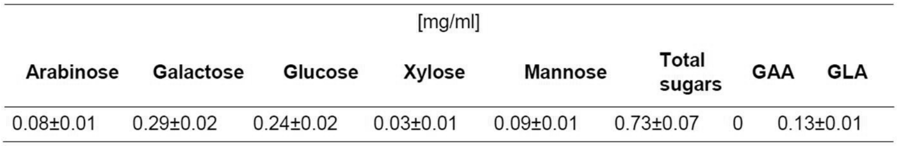
Figure 7.1: Water hyacinth fibres (stalk)

Table 7.2: a) Chemical composition of WH measured by HPAEC after H_2SO_4 hydrolysis; b) Monomeric sugars concentration in the leachates measured by HPAEC after H_2SO_4 hydrolysis and uronic acids concentration in the leachates measured by CG after methanolysis [33]

a)

Cellulose		37.9
Hemicellulose		37.6
Lignin	[%]	6.6
Ash		16.8
Extractive		23.6

b)



[mg/ml]							
Arabinose	Galactose	Glucose	Xylose	Mannose	Total sugars	GAA	GLA
0.08±0.01	0.29±0.02	0.24±0.02	0.03±0.01	0.09±0.01	0.73±0.07	0	0.13±0.01

Table 7.3: Chemical composition of ordinary Portland cement CEM I 52.5R used in this study

Chemical composition	[%]
CaO	64.60
SiO_2	20.08
Al_2O_3	4.98
Fe_2O_3	3.24
K_2O	0.53
Na_2O	0.27
SO_3	3.13
MgO	1.98
TiO_2	0.30
Mn_2O_4	0.10
P_2O_5	0.74
Cl^-	0.05

7.2.2 Methods

7.2.2.1 Pre-treatment

A saturated solution of $Ca(OH)_2$, (water: $Ca(OH)_2$, 10:1) close to pH 12 is prepared. Fibres are dried at 60°C prior to pre-treatment. They are then soaked in a large amount of saturated solution of $Ca(OH)_2$ at 24h/60°C. Fibres are then washed several times and dried at 60°C.

7.2.2.2 *Water absorption*

Water absorption (WA) measurements aim to determine the amount of water absorbed by each fibre when they are soaked in water for 24h and 48h at room temperature. Prior to measurement, the fibres are dried at 105°C for 24 hours. This method is applied six times for each fibre, with and without pre-treatment. The WA is calculated using an equation 4.1.

7.2.2.3 *Mass loss*

Fibres are dried and weighed before pre-treatments. After pre-treatments, the fibres are washed twice to remove calcium hydroxide and sugars. Filter papers (⌀ 120 mm) are used to prevent the loss of the fibres. The treated fibres and the filtered paper were dried at 105°C and weighted. Then, the mass loss is calculated and compared for each treated fibre. This method makes it possible to see the evolution of the fibre’s mass during pre-treatment due to eliminating sugars, wax and oil.

7.2.2.4 *SEM*

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses are performed using a Phenom Pro X scanning electron microscope to observe the surface of untreated and treated fibres in order to study the degradation of the fibres after pre-treatments. Micrographs are recorded using both scattering electron detectors at 15 kV with a spot of four.

7.2.2.5 *FT-IR*

Fourier Transform Infrared Spectroscopy (FT-IR) spectra are recorded using a Perkin Elmer Frontier FTIR with a GladiATR diffuse reflectance device. Eight scans are acquired with optical retardation of 0.25 cm and a resolution of 4 cm^{-1} from 500 to 4000 cm^{-1}. This method is used to characterise the effect of the pre-treatment at the fibres’ surface. Eight scans are acquired with optical retardation of 0.25 cm and a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}.

7.2.2.6 *Isothermal calorimetry*

Isothermal calorimetry is performed with a TAM Air Isothermal calorimeter at a constant temperature of 20°C. All untreated and treated fibres are mixed with OPC and water. The water/cement ratio is kept constant for all prepared mixes (w/c = 0.45), and the fibres/cement ratio was 0.075. An average of 36g of the mixture is used for one sample, with a particle size of the fibres 2 – 4 mm, and a large pot is used with a volume of 125 ml.

7.2.2.7 *Cement-fibre compatibility*

Several authors [14],[18],[134] have formulated different methods to measure the compatibility of wood species with OPC. In this study, an equation designed by Pasca et al. is used to assess the compatibility CX’ between different natural fibres and the OPC [139]. The equation is developed for cement-wood compatibility but can be suitable for other natural fibres due to the assumption that hydrated cement/wood/water mixtures and cement/fibres/water mixtures tend to have the same cement hydration behaviour as they have similar chemical composition [139]. The CX' factor can be determined using the equation 4.2.

7.3 Results and discussions

7.3.1 Physical behaviour

Figure 7.2 shows the water absorption measurements of the untreated and the treated WH fibres. The measurement is done for 24 and 48 hours to see the intake of water, which is essential in the production of cementitious materials for several reasons. Firstly, the high water uptake of the fibre can reduce workability during mixing and lower strength Secondly, the water, which is necessary for the hydration of the cement can be taken up by the fibres instead, which also lowers the strength of the composite.

As expected, WH has very high-water absorption, reaching 465% at 24 h and 562% at 48 h. This observation can be explained by the following mechanisms: first, by the porosity of the external wall of natural fibres where the quality of penetration is directly influenced (high porosity = high water absorption) [47]. Secondly, fibres' chemical composition WH contains large amounts of hemicellulose and cellulose (Table 7.2a) which are hydrophilic [184]. Thirdly, WH is a water plant, and contains large amounts of water in its structure and when the dry fibre is used, it will absorb an extreme amount of water [10]. WH is one of the few fibres with high water absorption, there is also Miscantus with very similar water absorption (300-400 %) compared to WH [50], which can be both used as a lightweight aggregate. Several examples of fibres that are used as a lightweight aggregate can be found in the literature. Miscanthus, peach and oil palm shells or rice fibres can be used in lightweight concrete [49–51,216]. Ismail and Jaeel used a lightweight aggregate from rice fibres measuring strength properties and water absorption of concrete in their research. It can be concluded that using a higher amount of fibres increases water absorption and decreases flexural and compressive strength [49]. Therefore, when creating a mix design with WH fibres this fact has to be taking in account. A smaller amount of fibres used in lightweight concrete or pre-treatment of fibres can be the solution to avoid decreasing strength and improve water absorption of fibres and concrete.

As mentioned previously, alkaline pre-treatment can be beneficial for natural fibres. Figure 7.2 shows the influence of the pre-treatment on WH. After using pre-treatment, water absorption values decrease by 30 % at 24 and 48 hours. It can be due to a relative increase in lignin content caused by decreasing cellulose and hemicellulose content making the fibres more hydrophobic overall [10]. Together with the residue of calcium hydroxide on the surface of the fibres, the water absorption can change behaviour (decreasing water absorption with pre-treatment). Due to the changing behaviour of water absorption and presumably the depression of cellulose and hemicellulose in WH fibres after pre-treatment, it is interesting to check to change fibre composition.

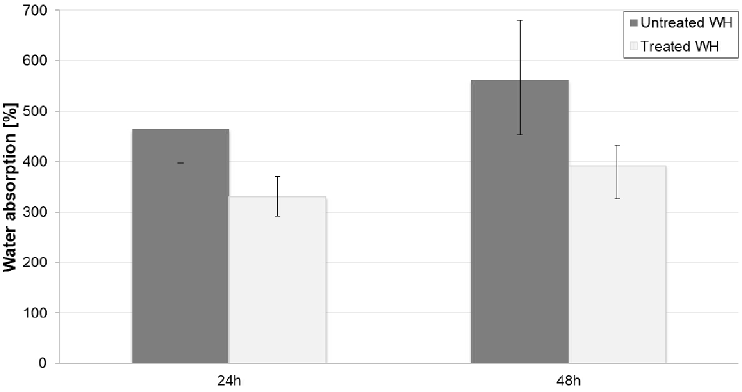


Figure 7.2: Water absorption of untreated and treated water hyacinth

To confirm the pre-treatment effect on the dissolution and elimination of some fibre components (i.e. hemicellulose, lignin), mass loss of WH fibres is measured after the pre-treatment. A significant weight loss, up to 15%, is obtained during pre-treatment, which also indicates a high extractive and hemicellulose content (Table 7.2a). The possible explanation may also be that this pre-treatment with higher temperature damages fibres more.

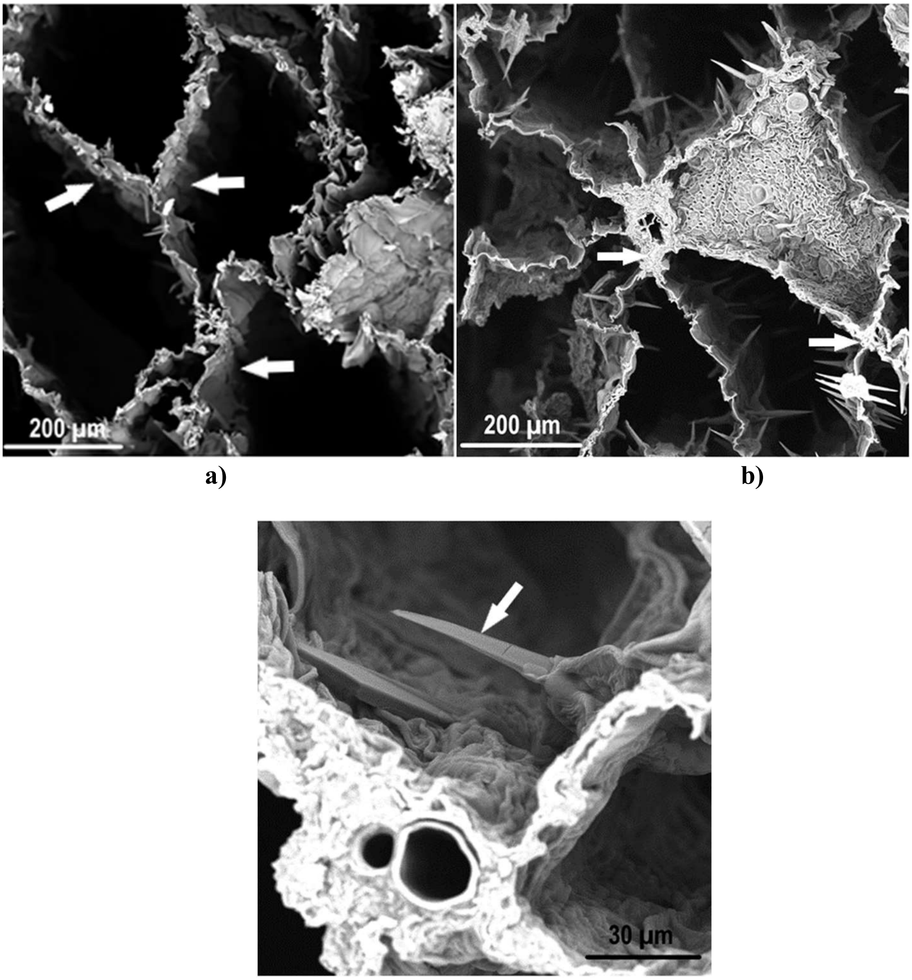
Results show a massive increase of water absorption during 24 h, which means that it has to be considered in a production line when using WH in cementitious materials. Cement for its hydration needs water, and usage of materials with high water absorption levels can cause a problem during the hydration of a final product. There are two options to be considered: the first option, the increasing amount of water in mix design, which can influence better cement hydration or the second option, is to use pre-treatment, where pre-treatment decreases water absorption level.

7.3.2 Microstructure analysis

In this study, Scanning Electron Microscopy is used to evaluate the effect of pre-treatment on cross-sections and surface of WH.

Figure 7.3a – c display a cross-section of petioles, which are composed of epidermal cells, fibre unite and aerenchyma tissue. In general, petioles are circles 10 – 15 mm in diameter long leaves, and their section is constituted of 20 – 40 fibre units (about 200 µm) [85,217]. A detailed internal structure of the petiole section is shown in Figure 7.3c. Fibre units of the petiole section are constructed by vascular bundles, enclosed by scarce parenchyma and aerenchyma tissue. Phloem and xylem are two parts of vascular bundles. Phloem is formed by sieve tubes and small companion cells, and xylem is composed of xylem vessels and tracheids, which both are empty and dried cells. Screletis, needle-like cells are shown in Figure 7.3c. Sclereties arise from aerenchyma cells and project into air space.

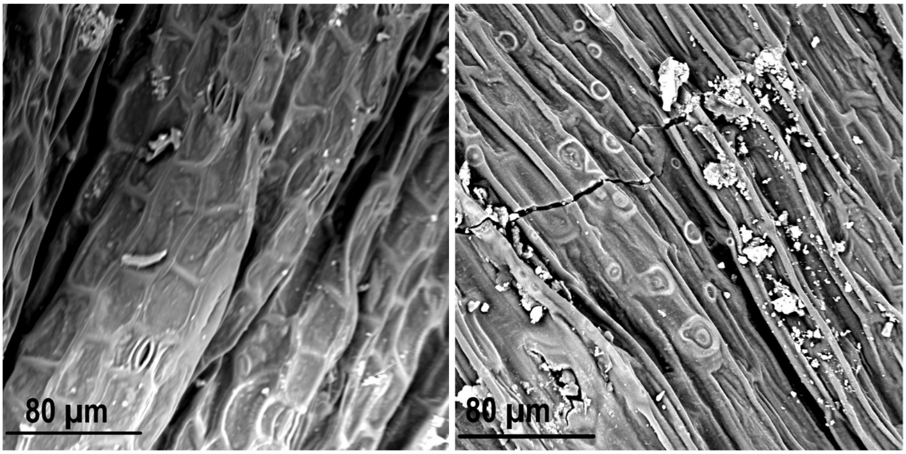
A comparison between the untreated and the treated WH fibres can be seen in Figures 7.4a, b. It can be observed that the untreated WH fibre has a smoother and uniform surface. On the other hand, the treated fibre is damaged on the surface, and the surface is slightly rougher after the pre-treatment. Traces of unknown particles can be noticed on the surface of these fibres. EDX analyses of the treated WH fibre (Figure 7.5) determined that these particles are residuum of calcium hydroxide, which can be expected when pre-treatment with calcium hydroxide is used.



a) **b)**

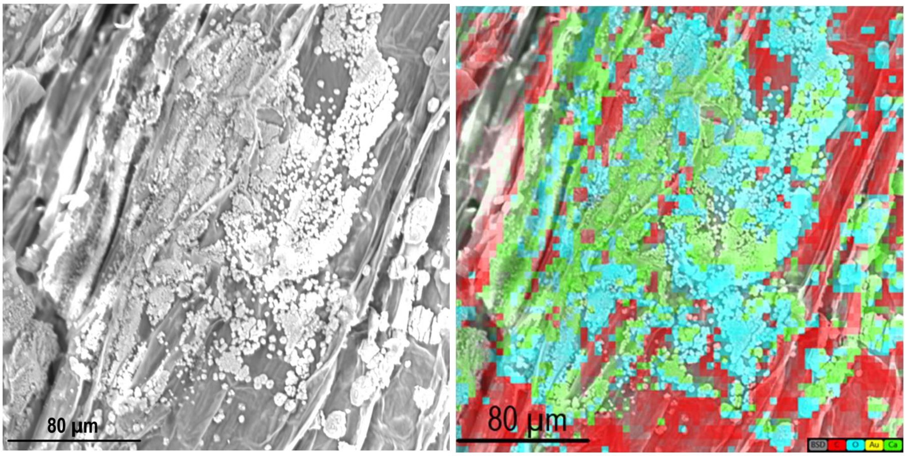
c)

Figure 7.3: Cross-section of WH (untreated) internal structure of the petiole using SEM: a) Aerenchyma tissue; b) Fibre unit of the petiole section; c) Detail of fibre unite of the petiole section



a) b)

Figure 7.4: SEM pictures of the surface of water hyacinth fibres before and after pre-treatment: a) Untreated fibre; b) Treated fibre



a) b)

Figure 7.5: EDX mapping of treated water hyacinth fibre: a) SEM picture; b) Picture from EDX mapping

SEM results show the residuum of calcium on the fibre surface and the rougher fibre surface compared to untreated WH, which can increase cement/fibre bonding. Due to damaged structure, calcium can also penetrate to pores, and a remaining and crystallised calcium can stay on the surface after drying [182,183]. The roughness can be helpful for the next step in the research when WH is used in lightweight concrete to increase the bonding strength between cement and fibre surfaces [212,218].

7.3.3 Characterisation of fibre composition

FT-IR spectroscopy can be used for a semi-quantitative composition analysis of cellulosic fibres [206]. Untreated and treated WH are analysed to determine any changes on the fibre's surface after pre-treatment.

From the literature is known that the most problematic part of the fibre is hemicellulose due to its negative effect on cement hydration. Moreover, wax and other impurities on the surface can affect the cement/fibre interaction [33].

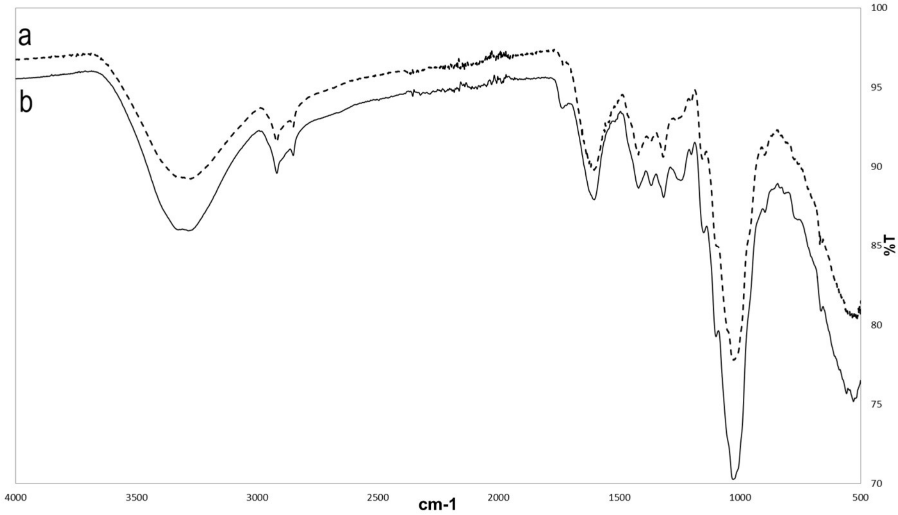


Figure 7.6: FT-IR spectra 4000 – 500 cm^{-1} of WH: Dashed lines: Untreated fibre (a); Full line: Treated fibre (b)

Table 7.4: Infrared absorption frequencies of untreated and treated coir fibres
[8,42,177,206]

Wavenumber [cm-1]	Vibration	Source
3300	O-H linked shearing	Polysaccharides
2980-2800	CH_2 symmetrical stretching	Wax
1750-1730	C=O stretching	Hemicellulose
1595	Aromatic ring vibration + C=O stretching	Lignin
1505	C=C aromatic symmetrical stretching	Lignin
1465	C-H deformation	Lignin
1425	CH_2 symmetric bending, C=C stretching in aromatic groups	Pectin, lignin, hemicellulose
1370	CH bending	Polysaccharides
1320	C-O aromatic ring	Cellulose
1240	C-O aril group	Lignin
1160	C-O-C asymmetrical stretching	Cellulose, hemicellulose
1035	C-O, C=C, C-O-C stretching	Cellulose, hemicellulose, lignin

Figure 7. 6 shows FT-IR spectra of the WH fibres before and after pre-treatment. The strongest signal is observed with untreated WH fibre, and the major peaks are summarised in Table 7.4. The spectra of the two WH fibres are similar to each other. Their main differences are seen with the peaks at 1750-1730 cm^{-1}, C=O stretching, corresponding to hemicellulose, as well as with the peak at 1505 cm^{-1}, C=C aromatic symmetrical stretching, corresponding to lignin. The peaks at 1465-1320 cm^{-1} correspond to hemicellulose, lignin, pectin and polysaccharides. It is evident from Figure 7.6, cellulose almost disappeared after WH was pre-treated.

The analysis of WH using FT-IR shows similar results as the chemical composition measured by HPAEC (Table 7.2a), even when FT-IR is measured on the fibres' surface. It indicates that the fibre is high in cellulose and hemicellulose. Furthermore, the application of alkali pre-treatments effectively removes hemicellulose and lignin.

7.3.4 Cement-water hyacinth composite

This study's primary goal is to see if WH fibres, as a lightweight aggregate, can be used in cementitious composites. It is known that WH can offer usage of two types of fibres: fibres from stems and fibres from leaves. In 2017 Kochova et al. [215] 3 different untreated WH fibres were used in preliminary tests. The first fibres were long fibres from stems, the second fibres were short fibres from stems to see any differences in strength due to the fibre distribution in matrix and possibly more leachate sugars from short fibres due to the larger surfaces. The third sets of fibres were short fibres from stems and leaves. In addition, different water/cement and fibre/cement ratios were used. Figure 7.7 shows one of the samples with short fibres from stems and leaves. The mixture was composed of cement, untreated fibres, and water to see the effect, which fibres would have on the composites' mechanical properties. WH had a strong effect on the cement hydration, and the non-hydrated part of cement in the composites can be seen. The study nevertheless concluded that WH could be a potential fibre used as a lightweight aggregate assuming pre-treatment is used.

Figure 7.7: The cement-water hyacinth composite [215]

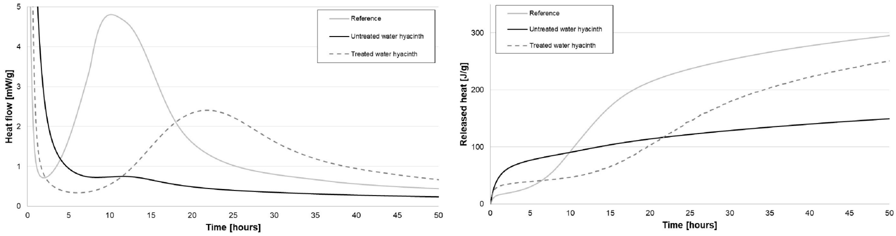
Overall, pre-treatment has a significant effect on WH, and good improvements can be seen through all obtained results. Therefore, WH can be considered to be used in lightweight concrete. Since WH is a water plant, there was an assumption that water absorption would be very high. This hypothesis is confirmed, whereas water absorption is nearly 500% at 24 h. Usage of the pre-treatment decreases water absorption values insignificantly by 30%. Differences between untreated and treated WH is also seen on the fibres' microstructure and surface. The residuum of calcium on the treated fibre surface is reviled with SEM as well as the rougher fibre surface. The application of alkali pre-treatments affects hemicellulose and lignin, which can be seen from FT-IR results. In sum, the pre-treatment significantly improves WH fibres, and water absorption must be considered as one of the most problematic fibres' behaviours.

Based on the research, which used pull-out tests to see bonding strength between cement and fibre surface [212,218] can be considered that pre-treatment contributes more than expected, helping cement/fibre matrix to a higher strength concrete.

Isothermal calorimetry was used to obtain and confirm the influence of untreated and treated WH fibres on cement hydration. The untreated and the treated fibres are added to the cement with water mixed and tested. By using the isothermal calorimetry data, cement-fibre compatibility can be calculated with Pasca's equation (4.2).

Figures 7.8a and b show the heat flow of treated and untreated WH samples compared to a reference (pure cement paste) Calorimetry results show a significant effect on cement hydration by WH fibres. The characteristic peak of cement hydration is situated at 12 hours after the test starts, indicating the formation of the reaction product of cement. The hydration peak of cement paste, where untreated WH are added, is insignificant lower intensities in comparison to the peak of the reference sample. (Figure 7.8a). The cement hydration peak with treated WH is lower in comparison with the peak of the reference sample and delayed around 11 hours. Although the heat flows show significant differences, the released heat has a similar trend to the reference sample. When untreated and treated WH is compared, it can be seen that at one point, the realised heats are the same after 24 hours. Nevertheless, the released heat of treated WH picks it up after that point and at 50 hours can be seen significantly higher released heat in comparison with untreated fibres. Those results indicate that using WH in cementitious materials may create a slight delay in cement hydration. Thus, the water content should be increased. There is also a slight delay with the hydration peak with treated WH; nevertheless, it is a vast difference compared to untreated WH. Similar results, where natural fibres are added to the cement matrix, are confirmed in previous studies.

One explanation of the results can be that dissolute organics from WH can poison cement, and therefore the cement hydration is hindered or slowed down [27,158]. Moreover, the extractive content (Table 7.2a), which is known from the literature to be mostly by-products of the hemicellulose degradation, is significant and has a strong effect during the hydration behaviour of the cement-fibre mix [11,147,150]. Another and most likely possible explanation is the very high water absorption (Figure 7.2), and therefore, there is no water for cement hydration left after it is absorbed into WH. Whereas, when pre-treatment is used, water absorption of WH fibres is decreased by 30%. A similar trend can be seen on the cement hydration, where treated WH has an increasing effect. The cement hydration peak of treated WH is higher than the cement hydration peak of untreated WH, suggesting some changes in the structure of fibres, as explained previously.



e) **b)**

Figure 7.8: Effect of water hyacinth fibres after and before pre-treatment on the cement hydration of OPC paste at 20°C: a) Heat flow, b) Released heat

For each fibre, untreated and treated the compatibility with cement was calculated and the data is depicted in Table 7.5. The improvement of cement-fibre compatibility after using pre-treatment on WH can be observed. After using pre-treatment, WH is moderately compatible with cement, and there is also a decrease in water absorption (Figure 7.5). Another explanation is the high content of extractive in WH fibres, which is known as a by-product of hemicellulose degradation and can cause a significant effect on the cement hydration [11,147,150].

Table 7.5: Cement-fibre compatibility of ordinary Portland cement CEM I 52.5R and untreated and treated fibres

Untreated water hyacinth	Treated water hyacinth
33	72

7.4 Conclusion

This study aims to characterise WH as an environmentally friendly potential fibre in cementitious building materials using several methods. Results show a promising potential for application in construction materials while using pre-treatment. The following conclusions can be drawn from the present study:

- Usage of natural fibres can be a good way to reduce our footprint and waste and be overall environmentally friendly compared to others. From the literature, it is known that natural fibres have some problems when used in cementitious materials. A good option to reduce those problems is to use pre-treatments. Different fibres need different pre-treatments, and sometimes a mechanical pre-treatment is enough. In other cases, a chemical pre-treatment is necessary.
- This study investigated two sets of WH fibres; untreated WH and treated WH fibres. Several tests were applied to obtain and understand differences between untreated and treated WH and its potential effect on the cement hydration and see if WH can be used as lightweight aggregate in lightweight concrete. Physical behaviour, microstructure, surface properties and cement-fibre compatibility are characterised in this study
- The WH characterisation establishes/reveals that WH is a very porous material due to its huge open cell walls compared to other fibres. Moreover, it is because WH is a water plant, which floats on the water surface. This fact can also explain the massive water absorption level. Using WH as a lightweight aggregate in cementitious building materials, water absorption must be considered while creating mix designs. Pre-treatments cause physical changes to the WH fibres. The analysis of fibres' composition using FT-IR spectroscopy was seen in the removal of hemicellulose and lignin. Morphological analyses done by SEM showed that the fibres roughness significantly changes with the pre-treatment. From this analysis, residues of calcium were discovered after the pre-treatment. The residuum can have a positive effect on cement hydration and cement/fibre bonding.

- Physical properties like water absorption or surface roughness can have an effect on processing cementitious materials as well as the CX' factor, which can quickly signal if fibre is good or not. This study obtained important information about the pre-treatment of WH, such as removal of hemicellulose, the roughness of fibres on their surfaces and increasing compatibility factor. Another factor to increase fibre/cement compatibility is to reduce porosity should be studied. More studies and testes are recommended for further development of cement-fibre composite or concrete.

Chapter 8

8 Conclusion and recommendations

8.1 Conclusions

8.1.1 Introduction

This thesis addresses alternative natural (waste) fibres as a replacement of wood in cement-wood composites and their influence on cement hydration. For many years wood fibres have been mixed with cement in various forms to make composite materials such as wood wool cement boards (WWCB) and wood cement-bonded boards (WCBB), collectively referred to as cement wood composites. The use of natural fibres as a sustainable alternative for reinforcements in cement-based materials has increased significantly. Using natural fibres as a reinforcement in cement-based composites is a challenge because natural fibres' microstructure and chemical composition can have a critical effect on cement hydration and thus the final composite properties.

8.1.2 Effect of saccharides on the hydration of ordinary Portland cement

Due to the data obtained from literature that sugars can leach out from wood and natural fibres and therefore slow down or even stop cement hydration, the influence of pure saccharides and the leachates of six natural fibres was investigated on the hydration cement hydration in Chapter 3. Three different types of sugars were used (fructose, glucose and sucrose), and the highest impact on the cement hydration had sucrose. This is due to that sucrose is a disaccharide combining glucose and fructose monomer units. One way to predict how fibre will react with cement is from leachates of fibres. Based on the number of monomeric sugars and uronic acids in leachates, the difference in the cement hydrations could be seen. A higher number of those compounds can be correlated with lower total heat realised during cement hydration. Furthermore, the pH of the leachates can also be used as a correlation with the monomeric sugars and uronic acids and their influence. Therefore, when pH is low, the cement hydration will be slower.

8.1.3 Influence of alkaline pre-treatments on alternative natural fibres used in cement-fibre composites

Another investigation into introducing waste natural fibres to Cementous materials to be more eco-friendly was introduced in Chapter 3. The previous chapter stated that most natural fibres have problems with sugars and can slow down cement hydration. One of the possible ways to reduce this effect is to use pre-treatments. In this thesis, it was used pre-treatment using $Ca(OH)_2$. Four different natural fibres and three different pre-treatment conditions were selected. To see how effective each pre-treatment was, cement/fibre compatibility was calculated. The significant impact of pre-treatment was with oil palm fibres when from compatibility, the number was 13, and after pre-treatment, the number went to 78. There could also be seen improvement with coir fibre, not with calculated compatibility but with roughtnessing the fibre surface and removing unwanted substances from the surface.

8.1.4 Investigation of local degradation in wood stands and its effect on cement wood composites

Another investigation was with wood fibres. Indisputably, using natural waste fibres is a better way to reduce and create less of position; nevertheless, wood is and will be used in cementitious materials. Therefore, this investigation could bring some inside why are some wood wool fibres work, and others do not. The difference between two very similar, commercially produced spruce wood wool fibres batches showed that even though these two types of wood passed standard quality controls, they are significantly different in compatibility, mechanical properties, and microstructure. The investigation showed the degradation of fibres and their hemicellulose through leachate tests and SEM micrographs.

8.1.5 Using alternative waste coir fibres as a reinforcement in cement-fibre composites

To reduce an environmental footprint and, therefore, CO_2 emissions. Coir fibre was chosen to be used in cementitious materials replacing wood fibres. In Chapter 5 was investigated composite made from pre-treated coir fibres and cement. Due to the pre-treatment, the cement/fibre interaction (bonding strength) was increased. The most important results were compared to conventional WWCB and the coir composite, where bending strength, density and thermal conductivity were measured. In those entire tests, the coir composite was very close to conventional WWCB.

8.1.6 Water hyacinth as an alternative natural fibre in cement composites

Water hyacinth is one of the most interesting fibres to use in cementitious materials, especially in lightweight concrete. It is not a waste product but a pest with a huge environmental footprint. Water hyacinth is different from other tested fibres due to its different structure and water absorption. When fibre is used without pre-treatment, the influence of cement hydration is very significant; therefore, a pre-treatment using $Ca(OH)_2$ was used for this study.

8.2 Recommendations

This PhD project which is presented, was initiated to obtain knowledge of natural fibres, mostly natural waste fibres, to achieve producing more sustainable cement-fibre composite by replacing wood wool with eco-friendly fibres. The results, which are presented in this PhD study, indicate positive accomplishments. Nevertheless, further study is still needed to achieve even more positive results.

Recommendation for further investigation based on this study:

- Correlation between total sugar content and released heat and can be used to predict the retarding behaviour of fibres. Even the pH of the leachate of fibres can be used as a fast indicator of the cement-fibre compatibility, although it has to be studied.
- Saturated $Ca(OH)_2$ solution was used as pre-retreatment; therefore, it can be calculated how many times this solution can be used as a pre-treatment solution. For further investigation can also be used a less concentrated solution.
- The used pre-treated solution is can be then used as a part of a circular economy. When pre-treatment is applied, hemicellulose and lignin are partly removed from the solution. Therefore, extraction of those components and further use is a way of multilateral use of fibres.
- The current quality control methods for testing wood samples before producing WWCB are not suitable for characterising micro degradation, which can have a significant effect on its properties. As an alternative method on an industrial scale, cement/fibre compatibility and single-strand tensile tests are good indicators of degradation and could be used in the future in order to improve the existing quality controls of the wood prior to the manufacture of WWCB.
- The study presented in this thesis is based on a lab scale, and the results are not checked in real factory applications. Therefore, large scale tests of pre-treatment and production of coir composite are needed and can be even developed further.

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List of symbols and abbreviations

WWCB	wood wool cement board
WCBB	wood cement-bonded board
OPC	ordinary Portland cement
etc.	et cetera
i.e.	id est (that is)
e.g.	exempli gratia (for example)
et al.	et alia (and others)
NF	natural fibres
CNF	cellulose natural fibres
GHG	Greenhouse gas
Ct	weighted maximum temperature ratio
CH	maximum heat ratio
C_A	the compatibility factor
F_c	the wood-cement compatibility factor
Q_c	the wood-cement hydration reaction Q_c at 48 hours
Q_P	the neat cement reaction Q_c at 48 hours
CX′	the cross-compatibility index
HPAEC	high-performance anion-exchange chromatography
GC	gas chromatography
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
FT-IR	Fourier Transform Infrared Spectroscopy
WA	water absorption
GAA	galacturonic acid

GLA	glucuronic acid
EFB	empty fruit bunch
WA	water absorption
w/c	water/cement ratio
f/c	fibre/cement ratio
WH	water hyacinth
ø	diameter
PET	polyethylene terephthalates
PP	polypropylene
PVA	polyvinyl alcohol

Summary

This thesis addresses alternative natural (waste) fibres as a replacement of wood in cement-wood composites and their influence on cement hydration. For many years, in various forms, wood fibres have been mixed with cement to make composite materials such as wood wool cement boards (WWCB) and wood cement-bonded boards (WCBB), collectively referred to as cement wood composites. Recently, the use of natural fibres as a sustainable alternative for reinforcements in cement-based materials has increased significantly. Using natural fibres as a reinforcement in cement-based composites is a challenge because natural fibres' microstructure and chemical composition can have a critical effect on cement hydration and thus the final composite properties.

The thesis starts with a short introduction of cement-fibre composites, possible usage of new fibres and their problems flowing with possible solutions. In Chapter 2, an introduction of the history of cement-fibre composites with an emphasis on WWCB and an introduction of new materials (natural waste fibres) is presented. Chapter 3 deals with the influence of new natural fibres on the cement hydration reactions. To better understand the problems, the characterisation of different organic compounds present in fibres is obtained. Experimental results show that glucose, mannose and xylose in fibre leachates have a significant impact on the cement hydration, slowing the hydration for up to 2 days. To improve the properties of the natural fibres and make them suitable to be used as a reinforcement, several pre-treatments are investigated in Chapter 4. An alkaline pre-treatment is used due to many advantages. It does not produce unwanted by-products like acid pre-treatments do and can remove hemicellulose, lignin, wax and oil. Experimental results show that pre-treatment can significantly improve cement-fibre compatibility and modify the surface of the fibres. Chapter 5 identifies the parameters that influence WWCB quality like mechanical properties, wood microstructure, and cement/fibre compatibility. In Chapter 6, coir fibres are chosen as the most suitable natural fibre due to their low density and high thermal conductivity. Good cement/fibre compatibility and boards are produced. A comparison between a standard WWCB and a cement-coir composite shows that thermal and mechanical properties are very close. In Chapter 7, water hyacinth fibres are investigated. Water hyacinth is a pest and, in several countries, an enormous environmental problem, and there is a question about what to do with those fibres. One of the solutions can be to use it as a replacement for wood in cement-fibre composites.

List of publications

Publication written within this PhD project are listed below

ISI Journals

K. Kochova, K. Schollbach, F. Gauvin, and H. J. H. Brouwers, “Effect of saccharides on the hydration of ordinary Portland cement,” *Constr. Build. Mater.*, vol. 150, pp. 268–275, 2017.

K. Kochova, F. Gauvin, K. Schollbach and H. J. H. Brouwers, “Influence of alkaline pre-treatments on alternative organic fibres used in cement-fibre composites,” Submitted.

K. Kochova, F. Gauvin, K. Schollbach and H. J. H. Brouwers, “Using alternative waste coir fires as reinforcement in cement-fibre composites,” . *Constr. Build. Mater.*, vol. 231, 117121, 2019.

K. Kochova, V. Caprai, F. Gauvin, K. Schollbach, and H. J. H. Brouwers, “Investigation of local degradation in wood stands and its effect on cement wood composite,” *Constr. Build. Mater.*, vol. 231, 117201, 2019.

K. Kochova, F. Gauvin, K. Schollbach and H. J. H. Brouwers, “Water hyacinth as an alternative organic fibre in cement composites,” Submitted.

Conference proceedings

K. Kochova, F. Gauvin, K. Schollbach and H. J. H. Brouwers, “Utilization of alternative organic fibres in cement fibres boards and an interaction effect”, Proceeding of the International Conference organized by Wuhan University of Technology, The 9th International Symposium on Cement and Concrete (ISCC 2017), November 2017, Wuhan.

K. Kochova, F. Gauvin, K. Schollbach and H. J. H. Brouwers, “Interaction effect of organic fibres on the cement hydration”, Proceeding of the International Conference organized by Brno University of Technology, Non-Traditional Cement and Concrete, ISBN 978-80-214-5507-8, June 2017, Brno, Czech Republic.

K. Kochova, K. Schollbach and H. J. H. Brouwers, “Use of alternative organic fibres in cement composites”, Proceeding of the International Conference, 4th International Conference on Sustainable Solid Waste Management, June 2016, Limassol, Cyprus.

K. Kochova, K. Schollbach and H. J. H. Brouwers, “Use of alternative fibres in Wood Wool cement boards and their influence on cement hydration”, Proceeding of the International Conference, 19th International Conference on Building Materials (Ibausil 2015), September 2015, Weimar, Germany.

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This thesis addresses alternative natural (waste) fibres as a replacement for wood in cement-wood composites and their influence on cement hydration. For many years, in various forms, wood fibres have been mixed with cement to make composite materials such as wood wool cement boards (WWCB) and wood cement-bonded boards (WCBB), collectively referred to as cement wood composites. Recently, the use of alternative natural fibres, biowaste in particular, as sustainable alternatives for reinforcements in cement-based materials has increased significantly. Using natural fibres as a reinforcement in cement-based composites is a challenge because natural fibres' microstructure and chemical composition can have a critical effect on cement hydration and, thus, the final composite properties.

The thesis starts with a short introduction to cement-fibre composites, the possible usage of new fibres and their problems, followed by possible solutions. Then an explanation of the history of cement-fibre composites with an emphasis on WWCB and an introduction to new materials (natural waste fibres) is presented. The parameters influencing WWCB quality, like mechanical properties, wood microstructure, and cement/fibre compatibility, are identified to avoid problems during production process. Next, the influence of alternative natural fibres on the cement hydration reactions is studied. The characterisation of different organic compounds present in fibres is obtained to better understand the problems. Several pre-treatments are investigated to improve the properties of the natural fibres and make them suitable to be used as a reinforcement. An alkaline pre-treatment is used due to its many advantages. Experimental results show that pre-treatments modify the surface of the fibres, and can significantly improve cement-fibre compatibility.. Coir fibres are chosen as the most suitable natural fibre due to their low density and high thermal conductivity, good cement/fibre compatibility, and boards are produced. A comparison between a standard WWCB and a cement-coir composite shows that thermal and mechanical properties are very close. In addition, also water hyacinth fibres are selected to be investigated in more detail as potential fibre alternative. Water hyacinth is a pest and, in several countries, an enormous environmental problem, and there is a question about what to do with those fibres. One of the solutions can be to use it as a replacement for wood in cement-fibre composites.

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