

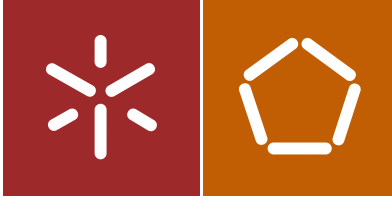


Universidade do Minho
Escola de Engenharia

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Microcrystalline Cellulose and Sisal Fibre
Reinforced Cementitious Composites

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Trabalho efetuado sob a orientação do
Professor Doutor Raul Figueiro

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RESUMO

Nas últimas décadas tem existido um crescente interesse em métodos alternativos de reforçar compósitos cimentícios. A utilização de fibras naturais como elemento de reforço tem sido bastante explorada ao longo dos anos, sendo que origina compósitos cimentícios com uma resistência ao impacto e à fissuração superior quando comparados com compósitos cimentícios comuns. Por outro lado, o uso de celulose microcristalina (CMC) também tem sido estudado, principalmente na última década, verificando-se que origina um aumento na resistência à compressão, assim como uma diminuição da fissuração causada por esforços provenientes de contração térmica e de resistência estrutural.

O principal objetivo deste trabalho foi estudar o comportamento de compósitos cimentícios reforçados à multiescala, através de CMC e de fibras de sisal. Para tal, procedeu-se à preparação de compósitos cimentícios com várias combinações de percentagens de CMC (0.2%, 0.5% e 0.75% em relação a cimento) e sisal (0.25% e 0.5% em relação a cimento) diferentes. Aos 28 dias, estes compósitos cimentícios reforçados com CMC e/ou sisal foram sujeitos a testes de resistência à flexão e à compressão. A incorporação de 0.5% CMC na matriz cimentícia resultou num aumento da resistência à flexão, assim como a adição de 0.5% sisal. Obteve-se um aumento da capacidade de carga pós-pico na matriz cimentícia quando fibras de sisal são adicionadas. Não se verificaram alterações significantes na resistência à compressão após incorporação de CMC e sisal.

A inclusão de CMC e fibras de sisal apresenta resultados promissores quando incorporados individualmente na matriz cimentícia. Em conjunto, CMC e sisal, não apresentam melhoria da resistência à flexão devido à natureza higroscópica de ambos. Portanto, um estudo mais aprofundado no efeito da hidratação destes elementos na matriz cimentícia deve ser efetuada.

Palavras-Chave: CMC, Sisal, Surfactante, Reforço, Compósito Cimentício

ABSTRACT

In the past few decades, there has been a growing interest in alternative methods of reinforcing cementitious composites. The use of natural fibres as a reinforcing element has been significantly explored over the years as it originates cementitious composites with superior impact and crack strength when compared with plain cementitious composites. On the other hand, the use of microcrystalline cellulose (MCC) has also been studied, particularly in the last decade, displaying an increase in compressive strength as well as a decrease in cracking caused by stresses due to thermal contraction and structural restraint.

The main objective of this research work was to study the behaviour of cementitious composites reinforced at multiscale with MCC and sisal fibres. In order to do so, cementitious composites were prepared with several different percentage combinations of MCC (0.2%, 0.5% and 0.75% w.r.t. cement) and sisal fibres (0.25% and 0.5% w.r.t. cement). At 28 days, these MCC and/or sisal reinforced cementitious composites were subjected to flexural and compressive strength testing. The incorporation of 0.5% MCC in the cementitious matrix resulted in an increase in flexural strength. Furthermore, the incorporation of 0.5% sisal in the cementitious matrix also showed an increase in flexural strength. An increase in the post peak load capacity was obtained with the addition of sisal fibres in cementitious matrix. There is no significant change in compressive strength after incorporation of sisal fibres and mcc together in cementitious matrix

The findings show that the inclusion of MCC and sisal fibres show promising results when incorporated individually in the cementitious matrix. Together, MCC and sisal do not show any improvement in flexural strength due to the hygroscopic nature of both, therefore, a more detailed study should be conducted in the hydration effect of these elements in the cementitious matrix.

KEYWORDS: MCC, SISAL, SURFACTANT, REINFORCEMENT OF CEMENTITIOUS COMPOSITES

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ABBREVIATIONS, SYMBOLS AND ACRONYMS LIST

CEN	European Committee for Standardization
cm	centimetre
CNT	Carbon Nanotube
CTAB	Cetyltrimethylammonium Bromide
CV	Coefficient of Variation
EN	European Norm
g	Grams
g/cm ³	Gram per cubic centimetre
G _F	Fracture Energy
Improv.	Improvement
km	Kilometre
kN	Kilo Newton
LM	Linear Mass
MCC	Microcrystalline Cellulose
ml	Millilitre
mm	Millimetre
mm ³	Cubic millimetre
MPa	Mega Pascal
N	Newton
N/mm	Newton per millimetre
nm	nanometre
NP	Portuguese norm
SP	Superplasticizer
TBP	Tributyl phosphate
UV	Ultraviolet
w.r.t.	With regards to
µm	micrometre
%	Percentage

Chapter 1 - INTRODUCTION

1.1. Scope

The construction industry is greatly responsible for the depletion of non-renewable resources. Therefore, research regarding the use of natural and renewable materials, such as natural fibres and cellulose which can be found in plants, is needed (S. Thomas et al., 2008).

Concrete, one of the most used materials on the planet, is known for its high compressive strength and low tensile strength. The combined use of concrete and steel reinforced bars has resolved the low tensile strength problem, as well as added to the compressive strength. Unfortunately, reinforced concrete is highly permeable which can lead to steel corrosion and therefore destruction of the concrete. Furthermore, steel is an expensive material, has high energy consumption and comes from a non-renewable resource (Torgal F. et al., 2011).

1.2. Motivation

For the reasons stated above, the idea of using natural fibres (NF) as a reinforcing element, either substituting or complementing steel, has been significantly explored over the years. Natural fibres in addition to being renewable also have good mechanical properties, low cost and are recyclable (Ramakrishna G. et al., 2005).

Natural fibres are constituted by several cellulose microfibrils, where cellulose chains are arranged in distinct conformations. One of them, cellulose microcrystalline (MCC), is a crystalline conformation in which the cellulose chains are disposed in organized and repetitive arrays to form crystals. This material will also be object of study in this dissertation (Hoyos C. et al., 2013).

The use of NF as a reinforcing material for concrete has already been explored. Consequently, it is known that, by using this type of reinforcement both impact and crack strength are superior to common concrete (G. Ramakrishna et al., 2005).

The use of MCC as a reinforcing material for concrete has also been explored and has shown to lead to an increase in compressive strength (M.S. Mohammed et al., 2014) and a decrease in cracking caused by stresses due to thermal contraction and structural restraint (Hoyos C. et al., 2013).

1.3. Objective

The purpose of this dissertation is to expand the knowledge on the use of these materials, exploring the effect of adding different percentages of the combination MCC/NF in cementitious matrixes, producing a multiscale reinforced material.

It is expected that, in the event of cracking, the NF will act on a macro scale while the MCC acts on a micro scale attributing a better mechanical behaviour to the cementitious composite. Ultimately, the expected result is a better behaviour with the combination NF/MCC than would be expected when used individually.

1.4. Thesis Structure

This thesis is divided into five chapters and seven attachments.

Chapter 1, the present chapter, is the Introduction. It contains the scope, motivation and objectives of this thesis.

Chapter 2 contains the theoretical concepts involving the subject of this work, in order to establish a background on which this work could be based. Cementitious composites, microcrystalline cellulose and natural fibres (in particular sisal fibres) were characterized by both physical and mechanical properties.

In Chapter 3 the materials and methods used throughout this work are presented. The methods used were optical and UV analysis, tensile testing of sisal fibres, development of cementitious composites, workability testing and, flexural and compressive strength testing.

Chapter 4 contains the results obtained from the testing described in the previous chapter. This chapter also contains the analysis of the obtained results.

Chapter 5 is the conclusion of this research work, along with suggested future work possibilities.

Chapter 2 - LITERATURE SURVEY

2.1. Microcrystalline Cellulose

Cellulose is the stiffest and the strongest organic constituent in the fibre. Microcrystalline cellulose (MCC) is a purified partially depolymerised non-fibrous form of cellulose that occurs as a white, odourless and tasteless crystalline powder composed of porous particles. MCC can be made from any material that contains high levels of cellulose ranging from pure cellulose, commercial grade cellulose to lignocellulosic materials. MCC has well-known binding properties and has proven to be stable, safe and physiologically inert (Adel A. et al., 2011).

Properties, such as crystallinity, moisture content, surface area and porous structure, molecular weight and many others, differ when cellulose is obtained from different sources. Therefore, properties of MCC obtained from different sources can also be expected to differ. Hydrolysis can also affect the properties of the obtained MCC.

To obtain MCC, cellulose hydrolysis is needed. Cellulose hydrolysis can be accomplished using mineral acid, enzymes or microorganisms. The conventional method of manufacturing MCC is acid hydrolysis. Enzymatic methods are desirable because glucose, a useful by-product, is created but these methods are more expensive and create MCC products with lower crystallinity.

MCC is used in various fields such as pharmacy, cosmetics, food industry and plastic processing industry (Adel A. et al., 2011).

2.2. Fibres

Fibres can be classified by its nature (natural or synthetic), by distribution (randomly dispersed or grouped accumulations), or by the shape of the groups (isolated, in several geometric nets or tangled forming a fabric).

Natural fibres derive from natural sources such as plants (sisal, flax, jute and more), animals (silk, wool) and minerals (mineral wool, for example), while synthetic fibres, such as glass, steel, carbon and polypropylene fibres, are man-made fibres, made with the purpose of improving on the properties of natural fibres (Gonzalez J., 2007).

All the fibres mentioned have distinct properties and characteristics and possess many advantages and disadvantages over the different fibres.

2.2.1. Plant Fibres

Reinforcement using plant-based fibres, such as cotton, hemp, jute, flax, ramie, sisal, bagasse and many others, has shown significant improvement in the properties of cementitious composites. As these fibres are obtained from renewable sources and readily available, at relatively low cost, they have an advantage over synthetic fibres. The benefits from large scale utilization of plant-based natural fibres as raw materials for cementitious composites are immense in terms of environmental, energy and resource conservation (Onuaguluchi O. et al., 2016).

Natural fibres have a high tensile strength and low modulus of elasticity. Even so, their tensile performance can stand in a favourable manner with synthetic ones. One of the disadvantages of using natural fibres is that they have a high variation on their properties which could lead to unpredictable concrete properties (Mohammed M. et al., 2014; Swamy R., 1990). For example, the tensile strength decreases with an increase in fibre length. This can happen because the longer the fibre, the higher the probability of it containing a defect (e.g. kink bands) which could lead to premature failure when compared with shorter fibres. Pre-treatment of natural fibres was found to increase concrete performance. Pulping is one of the fibre treatments that improve fibre adhesion to the cement matrix and also resistance to alkaline attack (Li Z. et al., 2006).

Even though fibres are discontinuous and are most commonly randomly distributed throughout the cementitious matrix, because they tend to be more closely spaced than conventional reinforcing bars, they are better at controlling cracking.

The natural fibre studied in this dissertation is sisal (Bentur A. et al., 2007).

2.2.1.1. Sisal Fibres

Sisal, also known as *Agave Sisalana*, is a leaf fibre. Leaf fibres are coarse and hard fibres obtained from leaf tissues either by hand scraping after a beating/retting process or mechanical extraction. Owing to the relatively high strength, leaf fibres are typically used for the production of ropes, fabrics, carpets and mats (Onuaguluchi O. et al., 2016).

Table 1 and Table 2 shows the mechanical properties and constitution of sisal fibres, respectively.

Table 1 – Mechanical properties of sisal fibres (P.V. Joseph et al., 1999)

	Tensile Strength (MPa)	Young Modulus (GPa)	Elongation at break (%)	Density (g/cm ³)
Sisal	511 - 635	9.4 - 22	2 – 2.5	1.5

Table 2 - Sisal fibre composition (Klerk M., 2015)

	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Extractives (%)	Ash (%)
Sisal	73.11	11.0	13.33	1.33	0.33

Figure 1 shows a photograph of a sisal plant.



Figure 1 - Agave Sisalana plant

According to Silva and Rodrigues, the addition of sisal fibres into concrete reduced its compressive strength which they claimed due to its low workability making its microstructure not as dense as that without fibre reinforcement (Silva J. et al. 2007).

An experimental programme carried out on sisal fibre-reinforced cement confirmed the theoretical prediction of an increase in flexural strength – by a factor of more than three percent. These results were achieved with suitable choices of mix parameters and fibre incorporation techniques (Swift D. et al., 1979).

2.3. Composites

The term composite is fundamentally broad, it means any system of two or more material phases combined and working together whose mechanical performance and properties are designed to be superior than those of the constituent materials (Arboleda D. et al., 2014).

Composites have many advantages such as lightweight, high strength, corrosion resistance, high impact strength, dimensional stability, design flexibility, nonconductive, nonmagnetic, low thermal conductivity, durable (Premix, 2016).

2.3.1. Multiscale Composite

Multiscale composites contain reinforcements at varying scales. This allows different elements to work on different phases of the composites lifespan.

In recent years, the use of multiscale composites has drawn significant attention in the field of advance, high-performance materials. Most of the efforts in multiscale composites research have been focused on improving the matrix-dominated properties by dispersing CNTs in the bulk of the matrix (Kim M. et al., 2009).

Cementitious composites reinforced with microcrystalline cellulose, at a microscale, and sisal fibres, at a macroscale, were studied in this research work.

2.3.2. Cementitious Composite Matrix

Plain cementitious composites are characterized by high compressive strength but low tensile strengths and low tensile strain capacities (they are brittle materials) (Pakravan H. et al., 2011; Bentur A. et al., 2007). The cementitious matrix can be divided into two types depending on the aggregate it contains: mortar (cement, sand and water mix) and concrete (cement, sand, coarse aggregate and water mix) (Bentur A. et al., 2007).

The cementitious matrix type used throughout this research work is the mortar. As mentioned, sisal (a natural fibre) and MCC were introduced in cementitious matrixes with varying percentages.

2.3.2.1. Cementitious Composite Reinforced with Natural Fibres

The purpose of reinforcing cementitious composites with fibres is to improve the mechanical properties, in particular the behaviour after cracking has started. The post cracking toughness that the fibres produce in the material may allow more intensive use of such composites in building. The performance of fibre reinforced composites depends on the volume and the physical and mechanical properties of the fibre as well as the binding properties between matrix and fibre (Gonzalez J., 2007).

The main drawback to the use of natural fibres is the durability of these fibres in a cementitious matrix and also the compatibility between both phases (Agopyan V. et al., 2005).

The durability of natural fibre reinforced cementitious composites hinges on its ability to resist both external (temperature and humidity variations, sulphate or chloride attack, amongst others) and internal damage (compatibility between fibres and cement matrix, volumetric changes, and others). The degradation of natural fibres immersed in Portland cement is due to the high alkaline environment which dissolves the lignin and hemicellulose phases, thus weakening the fibre structure.

Durability of fibre reinforced cementitious composites can be improved if matrix modification and/or fibre modification is used. Matrix modification consists in using low alkaline concrete by adding pozzolanic by-products to Portland cement such as rice husk ash or fly ashes. Results

show that the use of ternary blends containing slag/metakaolin and silica fume are effective in preventing fibre degradation. Fibre modification consists in coating natural fibres to avoid water absorption and free alkalis. Recent findings report that a silane coating of fibres is a good way to improve the durability of natural fibre reinforced concrete.

Some authors have mentioned that the use of pulped fibres can improve durability performance while others have reported that the fibre extraction process can prevent durability reductions. The use of compression and temperature (120, 160 and 200 °C) can lead to an increase of fibre stiffness and a decrease of fibre moisture absorption (Torgal F. et al., 2011).

2.3.2.2. Cementitious Composite Reinforced with MCC

The effect of MCC particles on the properties of cement based composites have already been analysed. The mechanical properties and hydration process of cementitious composites were studied using flexural testing and thermogravimetric analysis, respectively. The results showed that the interactions between MCC particles, cement particles, hydration products and water, decreased the workability and delayed the hydration reaction; however, these interactions increased temperature during curing process and increased the hydration degree of cement composites (Hoyos C. et al., 2013).

Further study on cementitious composites reinforced with MCC has shown a reduction in weight as well as an increase in compressive strength. In addition, lower ratios of MCC have shown better results at early ages of hydration and reported higher compressive strength than plain cement mortar.

No interaction was reported between the fibres and cement constituents based on the performed analysis (Mohammed M. et al., 2014).

Chapter 3 - MATERIALS AND METHODS

3.1. Materials

All the materials used in this research work were provided by the civil engineering construction materials laboratory of University of Minho, Fibrenamic International Platform, chemical department and the Institute of Science and Innovation for Bio-Sustainability (IB-S). The preparation of the cementitious composites, as well as the mechanical testing, was done in the civil engineering construction materials laboratory of University of Minho.

3.1.1. Bonding Agent

The bonding agent used was Portland Limestone-Cement CEM II / A-L 42,5 R produced by SECIL, certified in accordance with NP EN 197-1. According to the SECIL catalogue, this product has great versatility, good workability and high strengths. This cement is grey and has lower hydration temperature and better workability than cement CEM I of the same strength class. One of the main characteristics is the quick development of strength (high early strength). Further characteristics of this material can be found in Attachment 1 (SECIL, 2004). The Portland cement used was provided by the civil engineering construction materials laboratory of University of Minho.

3.1.2. Aggregates

The aggregate used was standard sand marketed by SOCIETE NOUVELLE DU LITTORAL (SNL), from France. The sand is CEN certified in accordance with EN 196-1, conforming to ISO 679:2009. It is a natural sand, siliceous, clean and its particles are generally isometric and rounded in shape. It is dried, screened and prepared in a modern workshop which offers every guarantee in terms of quality and consistency. The sand is packaged in polyethylene bags each containing 1350 ± 5 g. Further characteristics of this material can be found in Attachment 2 (SOCIETE NOUVELLE DU LITTORAL, 2016). The sand used was provided by the Fibrenamic International Platform.

3.1.3. Water

Distilled water was used to develop the cementitious composite. The water was provided by the chemical department.

3.1.4. Microcrystalline Cellulose

The MCC used, in all experiments depicted in this thesis, was from cotton linters marketed by Avicel®. This is a high purity cellulose powder (approximately 50 µm particle size).

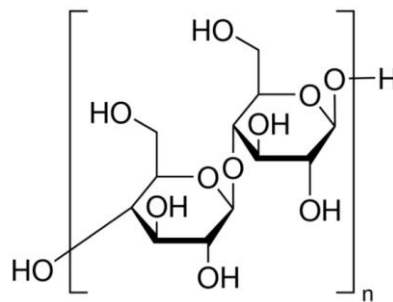


Figure 2 - Structural Formula of MCC [Avicel]

Figure 2 shows the chemical structure of MCC. The MCC used was provided by the Fibrenamic International Platform. Further characteristics of this material can be found in Attachment 3 (Avicel, 2008).

3.1.5. Sisal

The sisal fibres used were provided by the Fibrenamic International Platform. The fibres consisted of long strands with varying dimensions.

3.1.6. Other materials

In the development of the cementitious composites, chemicals were used to disperse the MCC (surfactants), as foam inhibitors and to increase fluidity in the cementitious composites (superplasticizer). The chemicals used were provided by the Fibrenamic International Platform.

3.1.6.1. Surfactants

The surfactants used were Pluronic F-127 and Cetyltrimethylammonium Bromide (C₁₉H₄₂BrN), also known as CTAB. Pluronic F-127 is a non-ionic surfactant and was marketed by SIGMA-ALDRICH. CTAB is a cationic surfactant and was marketed by Applichem Panreac. Figures 3 and 4 show the chemical structure of Pluronic F-127 and CTAB, respectively.

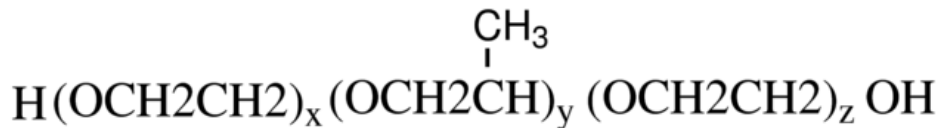


Figure 3 - Chemical Structure of Pluronic F-127 (SIGMA)

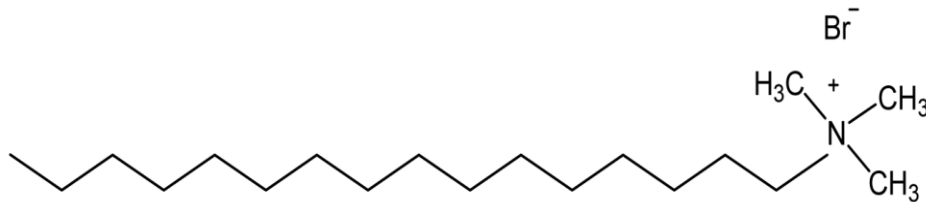


Figure 4 - Chemical Structure of CTAB (Ana Maria Carmona-Ribeiro et al., 2013)

3.1.6.2. Foam Inhibitor

The foam inhibitor used was Tributyl Phosphate (TBP) marketed by Chem-Lab.

3.2. Methods

All the methods used throughout this research work are described below.

3.2.1. Optical Analysis

An Olympus BH-2 microscope was used to perform the optical analysis. Both MCC and sisal fibres were subjected to optical analysis.

3.2.1.1. MCC without Surfactant

The percentages of MCC analysed were 0.4%, 1.0% and 1.5% MCC w.r.t. 10 ml of water. The quantities of MCC were calculated and are presented on Table 3.

Table 3 - Amount of MCC

Percentage of MCC	Quantity in 10 ml of water
0.4%	0.04 g
1.0%	0.1 g
1.5%	0.15 g

The three samples were prepared 48 hours in advance to allow the MCC time to settle. The quantities shown above were weighed and introduced into test tubes along with 10 ml of water, sealed and lightly shaken. Before optical analysis, all samples were placed in ultrasonic cleaner for 30 minutes. A drop from each sample (0.4% MCC, 1.0% MCC and 1.5% MCC w.r.t. water) were put on microscope slides and analysed with the microscope.

3.2.1.2. MCC with Pluronic F-127

The percentage of Pluronic F127 used was 20% w.r.t. MCC. The quantities of Pluronic F127 were calculated and are presented on Table 4.

Table 4 - Amount of MCC and Pluronic F127

Percentage of MCC	Quantity of MCC w.r.t. 10 ml of water	Quantity of 20% Pluronic F-127 w.r.t. MCC
0.4%	0.04 g	0.008 g
1.0%	0.1 g	0.02 g
1.5%	0.15 g	0.03 g

The quantities of MCC shown above were weighed and introduced into test tubes along with 10 ml of water, sealed and lightly shaken. After 48 hours, the corresponding quantities of Pluronic F127 were added to the test tubes, sealed and lightly shaken. Before optical analysis, all samples were placed in ultrasonic cleaner for 30 minutes. A drop from each sample were placed on microscope slides and viewed with the microscope.

3.2.1.3. MCC with CTAB

As there was not sufficient information on the optimal percentages of CTAB to MCC, the optical analysis of MCC with CTAB was done in three phases (Table 5):

Table 5 - Three phases analysed

Phase 1	Percentage of CTAB constant (20% CTAB w.r.t. MCC) and three different percentages of MCC (0.4%, 1.0% and 1.5% w.r.t. water)
Phase 2	Percentage of MCC constant (1.0% MCC w.r.t. water) and four different percentages of CTAB (40%, 60%, 80% and 100% w.r.t. MCC)
Phase 3	Percentage of CTAB constant (40% CTAB w.r.t. MCC) and three different percentages of MCC (0.4%, 1.0% and 1.5% w.r.t. water)

Phase 1 – Varying MCC + 20% CTAB

The percentage of CTAB used was 20% w.r.t. MCC. The quantities of CTAB were calculated and are presented on Table 6.

Table 6 - Amount of MCC and CTAB

Percentage of MCC	Quantity of MCC	Quantity of CTAB
0.4%	0.08 g	0.016 g
1.0%	0.2 g	0.04 g
1.5%	0.3 g	0.06 g

The quantities of MCC shown above were weighed and introduced into test tubes along with 20 ml of water, sealed and lightly shaken. After 48 hours, the corresponding quantities of CTAB were added to the test tubes, sealed and lightly shaken. Before optical analysis, all samples were placed in ultrasonic cleaner for 30 minutes. A drop from each sample were placed on microscope slides and viewed with the microscope.

Phase 2 – 1% MCC + Varying CTAB

The percentage of MCC used was 1.0% w.r.t. water (0.1 g). The quantities of CTAB were calculated and are presented on Table 7.

Table 7 - Amount of CTAB

Percentage of CTAB	Quantity of CTAB
40%	0.04 g
60%	0.06 g
80%	0.08 g
100%	0.1 g

The quantity of MCC, 0.1 g, was weighed and introduced into four test tubes along with 10 ml of water, sealed and lightly shaken. After 48 hours, the quantities of CTAB shown on the table above were added to the test tubes, sealed and lightly shaken. Before optical analysis, all samples were placed in ultrasonic cleaner for 30 minutes. A drop from each sample were placed on microscope slides and viewed with the microscope.

Phase 3 – Varying MCC + 40% CTAB

The percentage of CTAB used was 40% w.r.t. MCC. The quantities of CTAB were calculated and are presented on Table 8.

Table 8 - Amount of MCC and CTAB

Percentage of MCC	Quantity of MCC w.r.t. 10 ml of water	Quantity of CTAB w.r.t. MCC
0.4%	0.04 g	0.016 g
1.5%	0.15 g	0.06 g

The quantities of MCC shown above were weighed and introduced into test tubes along with 10 ml of water, sealed and lightly shaken. After 48 hours, the corresponding quantities of CTAB were added to the test tubes, sealed and lightly shaken. Before optical analysis, all samples were placed in ultrasonic cleaner for 30 minutes. A drop from each sample were placed on microscope slides and viewed with the microscope.

3.2.1.4. Sisal Fibres

The sisal fibres were cut into lengths of 20 mm in order to facilitate viewing. The fibres were placed on microscope slides and viewed with the microscope.

3.2.2. UV Analysis of MCC

The UV-VISIBLE Recording Spectrophotometer (UV-2401PC) was used to perform the UV analysis of MCC.

In addition to the samples, to perform this analysis it is necessary to make reference samples. The reference samples are aqueous solutions containing the same concentration of surfactant used to disperse the MCC in order to remove any peak generated by the reference samples during UV-Vis analysis. These reference samples were made 48 hours before UV analysis. In the case where no surfactant was used, the reference sample was distilled water.

After all the system checks were concluded, the type of experiment mode was chosen (Spectrum). Spectrum mode is used for wavelength scanning over a continuous wide range. Mode chosen it was necessary to set up the acquisition patterns, such as wavelength range (1000 to 190 nm) and measuring mode (Absorption). Next the baseline was created by filling the two cells with the reference samples, putting the cells in the respective holders and clicking Baseline on the computer (Figure 5).

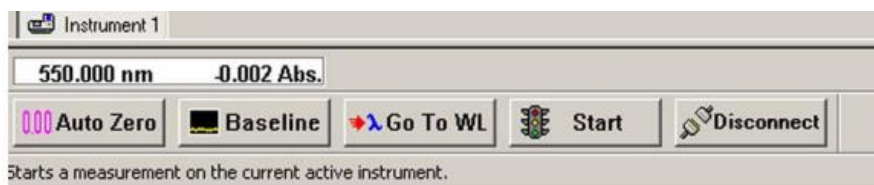


Figure 5 - Print from UV-2401PC

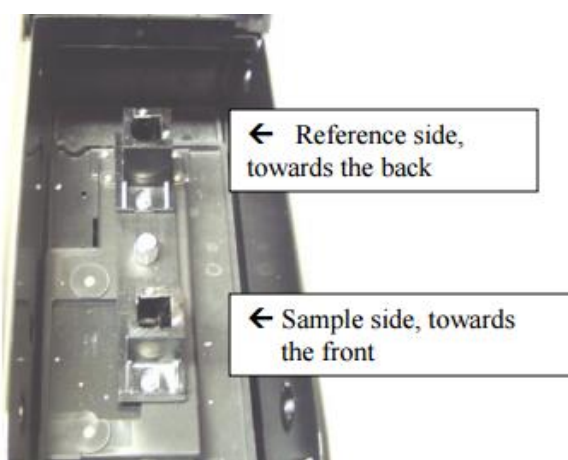


Figure 6 - Cells and cell holder

Baseline done, the sample cell was filled (Figure 6) with the first sample (reference cell was not touched) and by clicking on Start, the spectrum started getting collected. This process, creating baseline then spectrum, was repeated every time a reference sample was changed.

3.2.3. Tensile Behaviour of Sisal Fibres

To determine the tensile behaviour of sisal fibre three steps were followed:

Step 1 – Sample preparation;

Step 2 – Determination of the linear mass;

Step 3 – Tensile testing.

Step 1 – Sample preparation

50 samples of sisal fibres were cut into 20 cm lengths. Each sample was labelled, from 1 to 50, as presented in figures 7 and 8.

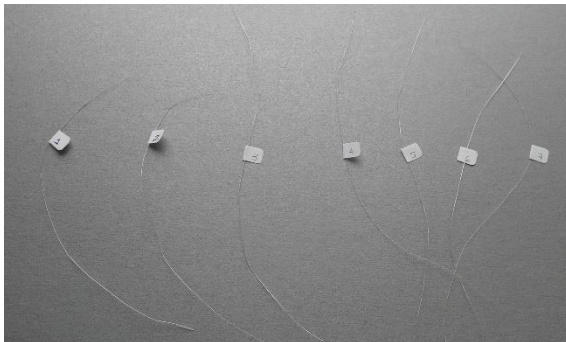


Figure 7 - Samples 1 to 7

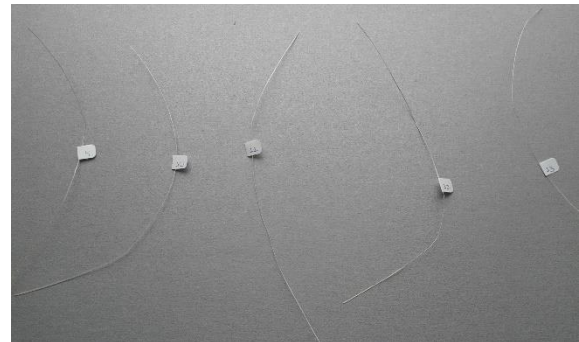


Figure 8 - Samples 9 to 13

Step 2 - Linear Mass Determination

Having prepared the samples, the next step was to determine the linear mass (LM) of each fibre (Eq. 1). For that reason, each fibre was weighed and had its length in tension measured. The length of the fibre in tension was obtained with the use of a measuring in tension equipment (Figure 9).

$$LM (Tex) = \frac{\text{Fibre weight (g)}}{\text{Length of fibre in tension (km)}} \quad (\text{Eq. 1})$$



Figure 9 – Equipment used to measure in tension

Linear mass of the samples was determined considering the results obtained. Linear mass was determined because it is one of the parameters needed, to introduce in the software, in order to obtain tensile strength of the fibres.

Step 3 - Tensile testing

The equipment used for tensile testing was the H100KS Hounsfield Universal Testing Instrument (Figure 10). The samples were placed, one by one, in the clamps (Figure 11 and 12) and after the introduction of the linear mass of the particular sample, the testing began.



Figure 10 - Tensile strength testing machine

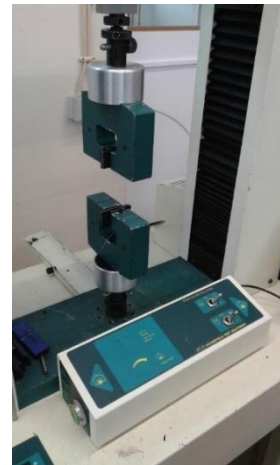


Figure 11 - Sample in use

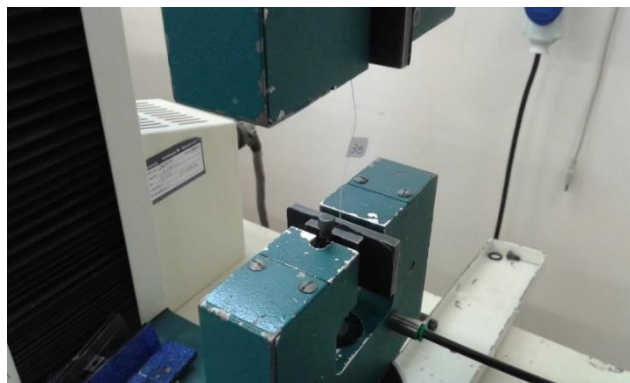


Figure 12 - Sample before testing

3.2.4. Development of Cementitious Composites

The objective of this research work was to analyse if the addition of MCC and sisal fibres into a cementitious composite would show improvement over a plain cementitious composite. In order to do so three types of cementitious composites were analysed, ones containing MCC, others containing sisal and still others containing sisal and MCC. The intention was to study which samples had the best results and try to understand why.

Several percentages of MCC (0.2%, 0.5% and 0.75% w.r.t. cement) and sisal (0.25% and 0.5% w.r.t. cement) were studied, as well as different surfactants. Because MCC is insoluble in water the use of a surfactant came into question. So, for each cementitious composite combination used there were three different samples, one containing Pluronic F-127, one containing CTAB and another with no surfactant. Sisal fibres were cut into segments with 20 mm of length.

Therefore, twenty-seven samples were analysed. One plain mortar, eight without surfactant, eight with Pluronic F-127 and ten with CTAB. 20% of Pluronic F-127 w.r.t. MCC was used as it is the optimal percentage according to literature. The percentage of CTAB required some analysis as there does not exist sufficient literature on the matter. 100% CTAB was used before optical and UV analysis could be accomplished and as the cementitious composites (with 100% CTAB) appeared visually very porous, when 40% CTAB showed the best results in UV analysis, the percentage of CTAB was altered from 100% to 40%. Tables 9, 10, 11 and 12 contain the samples studied according to surfactant use and percentage combination used of MCC and sisal.

Table 9 - Samples studied without surfactant

No Surfactant
01. Plain cementitious mortar
02. Cementitious mortar reinforced with 0.2% MCC w.r.t. cement
03. Cementitious mortar reinforced with 0.5% MCC w.r.t. cement
04. Cementitious mortar reinforced with 0.75% MCC w.r.t. cement
05. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement
06. Cementitious mortar reinforced with 0.5% Sisal w.r.t. cement
07. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.2% MCC w.r.t. cement
08. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.5% MCC w.r.t. cement
09. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.75% MCC w.r.t. cement

Table 10 - Samples studied with 20% Pluronic F-127

20% Pluronic F-127 w.r.t. MCC
01. Cementitious mortar reinforced with 0.2% MCC w.r.t. cement
02. Cementitious mortar reinforced with 0.5% MCC w.r.t. cement
03. Cementitious mortar reinforced with 0.75% MCC w.r.t. cement
04. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement
05. Cementitious mortar reinforced with 0.5% Sisal w.r.t. cement
06. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.2% MCC w.r.t. cement
07. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.5% MCC w.r.t. cement
08. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.75% MCC w.r.t. cement

Table 11 - Samples studied with 100% CTAB

100% CTAB w.r.t. MCC
01. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.2% MCC w.r.t. cement
02. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.5% MCC w.r.t. cement

Table 12 - Samples studied with 40% CTAB

40% CTAB w.r.t. MCC
01. Cementitious mortar reinforced with 0.2% MCC w.r.t. cement
02. Cementitious mortar reinforced with 0.5% MCC w.r.t. cement
03. Cementitious mortar reinforced with 0.75% MCC w.r.t. cement
04. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement
05. Cementitious mortar reinforced with 0.5% Sisal w.r.t. cement
06. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.2% MCC w.r.t. cement
07. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.5% MCC w.r.t. cement
08. Cementitious mortar reinforced with 0.25% Sisal w.r.t. cement + 0.75% MCC w.r.t. cement

3.2.4.1. Cementitious Composites without Surfactant

The materials used to develop this part of the work include: Portland cement, sand, water, MCC and sisal fibres. The ratio used for cement/sand/water was 1/3/0.5.

Table 13 contains the quantities of the materials used in the samples. The sisal fibres used had 20 mm of length.

Table 13 - Quantities of each material for sample preparation

Description	Quantity	Description	Quantity w.r.t. cement
Cement	450 g	0.2% MCC	0.9 g
Water	225 ml	0.5% MCC	2.25 g
Sand	1350 g	0.75% MCC	3.375 g
0.25% Sisal w.r.t. cement	1.125 g	0.5% Sisal	2.25 g

Dispersion of MCC in water

Samples containing MCC had to be prepared 48 hours in advance, in order to allow MCC particles to swell in the water. Accordingly, the quantities of MCC required were added to the distilled water (225 ml), sealed and mixed in the magnetic stirrer for 15 minutes.

If the sample contained MCC, before mixing the mortar, the water containing MCC previously prepared, was mixed with the magnetic stirrer for fifteen minutes followed by fifteen minutes in the ultra-sonication machine. Subsequently, the water was kept on the magnetic stirrer until it was time to add to cement.

Preparation of cementitious composites

All the samples were prepared in a similar manner, differing only in the use or not of MCC and sisal fibres. Using a Hobart mixer, the cement was mixed with the water (containing or not MCC, according to the sample being made), after which the sand was added, followed by the sisal fibre if required in the sample. The mortar was mixed for 3 minutes. Figure13 shows an image of the Hobart mixer used throughout this work.

*Figure 13 - Hobart mixer*

3.2.4.2. Cementitious Composites with Pluronic F-127

The materials used to develop this part of the work include: Portland cement, sand, water, MCC, sisal fibres, Pluronic F-127 and TBP. The ratio used for cement/sand/water was 1/3/0.5.

Table 14 contains the quantities of the materials used in the samples. The sisal fibres used had 20 mm of length.

Table 14 - Quantities of each material for sample preparation

Description	Quantity	Description	Quantity
Cement	450 g	0.2% MCC	0.9 g
Water	225 ml	0.5% MCC	2.25 g
Sand	1350 g	0.75% MCC	3.375 g
0.25% Sisal	1.125 g	0.5% Sisal	2.25 g
20% Pluronic F127 w.r.t. 0.2% MCC	0.18 g	50% TBP w.r.t. 20% Pluronic F127 (0.2% MCC)	0.1 ml
20% Pluronic F127 w.r.t. 0.5% MCC	0.45g	50% TBP w.r.t. 20% Pluronic F127 (0.5% MCC)	0.25 ml
20% Pluronic F127 w.r.t. 0.75% MCC	0.675 g	50% TBP w.r.t. 20% Pluronic F127 (0.75% MCC)	0.35 ml

Dispersion of MCC/Pluronic F-127 in water

The samples that contained MCC had to be prepared in advance in order to allow the MCC particles to swell in the water. Accordingly, 96 hours before making the samples the quantities of MCC required were added to the distilled water (225 ml), sealed and mixed in the magnetic stirrer for 15 minutes. After 48 hours, the required quantities of Pluronic F-127 and TBP were added to the MCC infused water and mixed in the magnetic stirrer for fifteen minutes.

If the sample contained MCC, before mixing the mortar, the water containing MCC previously prepared, was stirred with the magnetic stirrer for fifteen minutes followed by fifteen minutes in the sonication machine. Subsequently, the water was kept on the magnetic stirrer until it was time to add to cement.

If the sample did not contain MCC, 48 hours before making them, Pluronic F-127 and TBP were added to the water (225 ml) and mixed in the magnetic stirrer for fifteen minutes. This process was done in order to create consistency in the samples.

Preparation of cementitious composites

All the samples were prepared in a similar manner, differing only in the use or not of MCC and sisal fibres. Using a Hobart mixer, the cement was mixed with the water (containing or not MCC and Pluronic F127, according to the sample being made), after which the sand was added, followed by the sisal fibre if required in the sample. The mortar was mixed for 3 minutes.

3.2.4.3. Cementitious Composites with CTAB

The materials used to develop this part of the work include: Portland cement, sand, water, MCC, sisal fibres, CTAB and TBP. The ratio used for cement/sand/water was 1/3/0.5.

Table 15 contains the quantities of the materials used in the samples. The sisal fibres used had 20 mm of length.

Table 15 - Quantities of each material for sample preparation

Description	Quantity	Description	Quantity
Cement	450 g	0.2% MCC w.r.t. cement	0.9 g
Water	225 ml	0.5% MCC w.r.t. cement	2.25 g
Sand	1350 g	0.75% MCC w.r.t. cement	3.375 g
0.25% Sisal w.r.t. cement	1.125 g	0.5% Sisal w.r.t. cement	2.25 g
40% CTAB w.r.t. 0.2% MCC	0.36 g	50% TBP w.r.t. 40% CTAB (0.2% MCC)	0.2 ml
40% CTAB w.r.t. 0.5% MCC	0.9 g	50% TBP w.r.t. 40% CTAB (0.5% MCC)	0.5 ml
40% CTAB w.r.t. 0.75% MCC	1.35 g	50% TBP w.r.t. 40% CTAB (0.75% MCC)	0.7 ml
100% CTAB w.r.t. 0.2% MCC	0.9 g	50% TBP w.r.t. 100% CTAB (0.2% MCC)	0.5 ml
100% CTAB w.r.t. 0.5% MCC	2.25 g	50% TBP w.r.t. 100% CTAB (0.5% MCC)	1.2 ml

Dispersion of MCC/CTAB in water

The samples that contained MCC had to be prepared in advance in order to allow the MCC particles to swell in the water. Accordingly, 96 hours before making the samples the quantities of MCC required were added to the distilled water (225 ml), sealed and mixed in the magnetic

stirrer for 15 minutes. After 48 hours, the required quantities of CTAB and TBP were added to the MCC infused water and mixed in the magnetic stirrer for fifteen minutes (Figure 14 and 15).



*Figure 14 – Sample 1 on magnetic stirrer
[0,4% MCC w.r.t. water]*



*Figure 15 – Sample 2 on magnetic stirrer
[1,0% MCC w.r.t. water]*

If the sample contained MCC, before mixing the mortar, the water containing MCC previously prepared, was mixed with the magnetic stirrer for fifteen minutes followed by fifteen minutes in the sonication machine. Subsequently, the water was kept on the magnetic stirrer until it was time to add to cement.

If the sample did not contain MCC, 48 hours before making them, CTAB and TBP were added to the water (225 ml) and mixed in the magnetic stirrer for fifteen minutes. This process was done in order to create consistency in the samples. The percentages of CTAB and TBP used were the lowest percentages used in the MCC samples (40% CTAB in regards to 0,2% MCC).

Preparation of cementitious composites

All the samples were prepared in a similar manner, differing only in the use or not of MCC and sisal fibres. Using a Hobart mixer, the cement was mixed with the water (containing or not MCC and CTAB, according to the sample being made), after which the sand was added, followed by the sisal fibre if required in the sample. The mortar was mixed for 3 minutes.

3.2.5. Flow Table Test

This test was done according to the norm EN 1015-3 with the objective of measuring the workability of the cement past. After well mixed the workability of the mortar was tested using the flow table test. The cementitious mixture was placed into the cylindrical mould in two layers taped ten times with a cylindrical rod. When the top layer was level with the top of the mould any excess was cleaned off. After lifting the cylinder, the mixture was allowed to spread on the table and, following fifteen lifts and drops of the table, the diameter of the cementitious mixture was measured twice, according to figures 16, 17, 18 and 19.



Figure 16 - Workability test



Figure 17 - Workability test



Figure 18 – Measuring workability

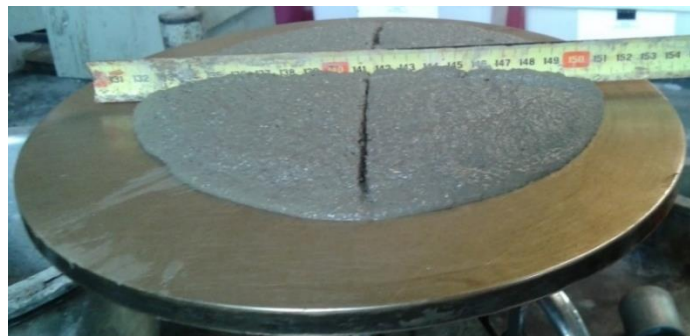


Figure 19 – Measuring workability

Some samples obtained less than 165 mm in the fluidity test so superplasticizer (SP) was added to increase fluidity. 0.5 ml of superplasticizer were added to the samples until fluidity was above 165 mm.

The fluidity test done, the mixtures were placed in moulds with $160 \times 40 \times 40 \text{ mm}^3$. The filled moulds were subjected to sixty blows in order to compact the mixture (Figure 20).



Figure 20 - Compacting machine

The samples were kept in a hydration chamber for 48 hours, after which they were demoulded (Figure 21 and 22) and placed in water for 26 days.



Figure 21 - Sample_04

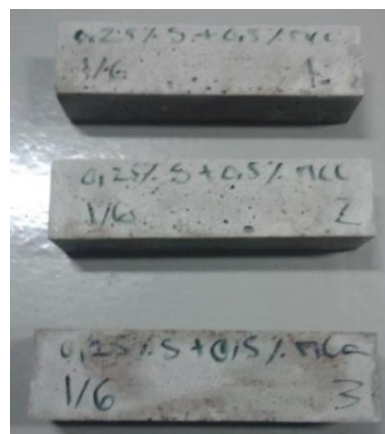


Figure 22 - Sample_05

3.2.6. Flexural Strength Testing

A LLOYD LR50K Plus machine was used to perform the flexural testing of the samples. This testing was done according to the procedures described in the norm EN 1015-11 (1999). Before testing, samples were weighed and two lines were drawn on the bottom face of the samples, on each side, 3 cm from the edge, as shown in Figure 23.



Figure 23 - Sample

These lines were drawn in order to facilitate the placement of the samples in the machine. Each sample was placed in the machine, coinciding the lines drawn with the two knife-edge points (distanced 10 cm from each other), as shown in the figure bellow. After well placed (Figure 24), the samples were subjected to increasing loads at the midpoint of the sample until break occurred.



Figure 24 - Flexural testing

Maximum stress and strain were calculated on the incremental load applied. The results from the flexural testing were displayed in a graphical format with tabular results.

3.2.7. Compressive Strength Testing

The ELE AutoTest 2000 BS compression machine (Figure 25 and 26) was used to perform the compressive testing of the samples. This testing was also done according to the norm EN 1015-11 (1999), mentioned above.



Figure 25 - Compressive machine



Figure 26 - Compressive machine (close-up)

As the samples were already subjected to flexural testing, two parts of each sample (Figure 27) were available for compressive testing.



Figure 27 - Sample 2.2 after flexural testing

Each sample was placed in the compressive machine, as shown in Figure 28, and subjected to increasing loads until break occurred (Figure 29).



Figure 28 – Sample in the compressive machine



Figure 29 - Sample post break

Chapter 4 - RESULTS AND BEHAVIOUR ANALYSIS

4.1. Optical Analysis

4.1.1. MCC without Surfactant

The analysis was done using the 3,3x eye piece and the objective at 4x. The results are shown in Figures 30, 31 and 32.

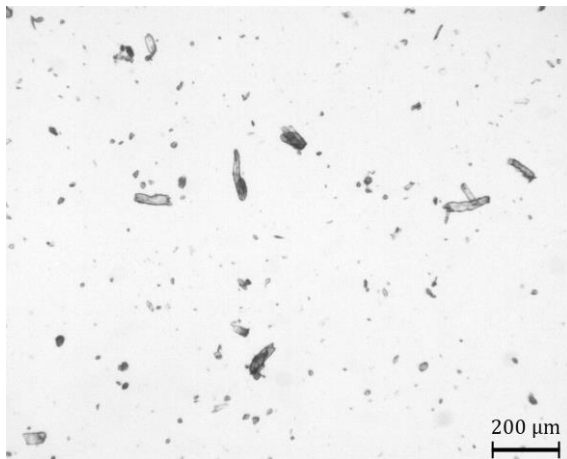


Figure 30 - 0.4% MCC

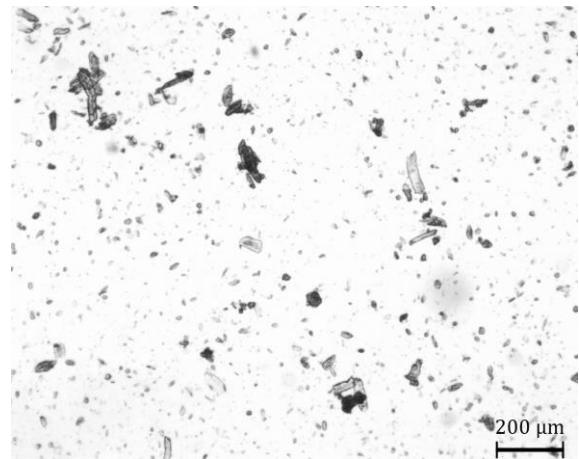


Figure 31 - 1.0% MCC

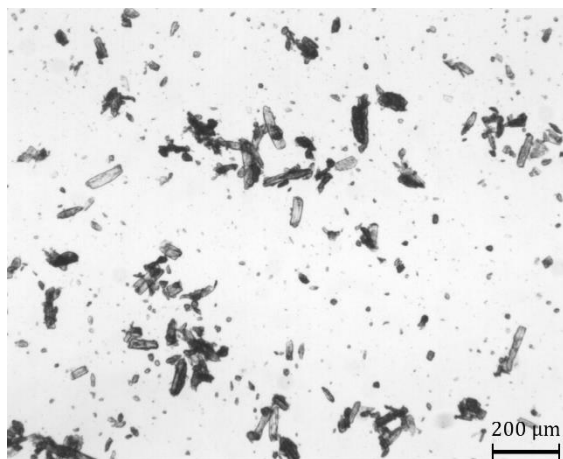


Figure 32 - 1.5% MCC

According to the figures the sample containing 1.5% MCC has a higher agglomeration of MCC particles while 0.4% MCC has a more disperse distribution. The MCC particles in Figure 31 (1.0% MCC w.r.t. water) seem more evenly distributed within the solution than the particles in Figure 32 (1.5% MCC w.r.t. water).

4.1.2. MCC with Pluronic F-127

The analysis was done using the 3,3x eye piece and the objective at 4x. The results can be viewed in figures 33, 34 and 35.

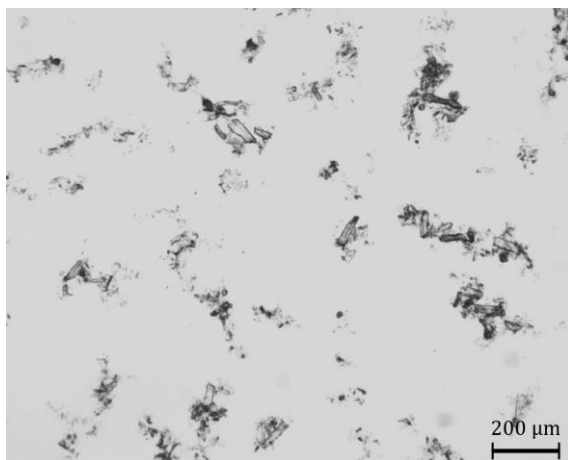


Figure 33 - 0.4% MCC + Pluronic F127

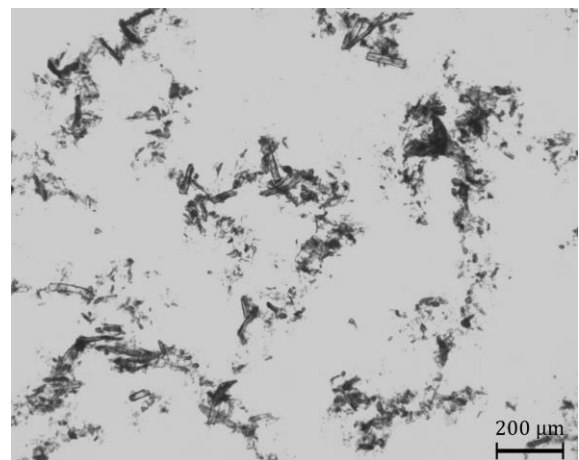


Figure 34 - 1.0% MCC + Pluronic F127

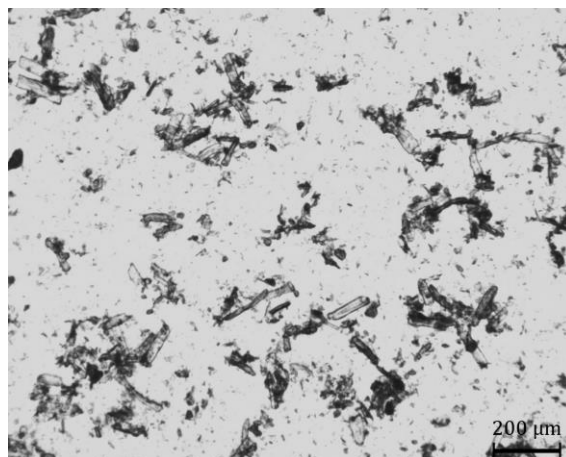


Figure 35 - 1.5% MCC + Pluronic F127

According to the figures, the samples containing 1.5% MCC have the highest agglomeration of MCC, although the sample containing 1.0% also has a high agglomeration, not much lower

than the 1.5% sample. Furthermore, Figure 35 (1.5% MCC) also has the higher number of disperse MCC particles.

4.1.3. MCC with CTAB

Phase 1 – Varying MCC + 20% CTAB

The analysis was done using the 1.67x eye piece and the objective at 10x. The results can be viewed in figures 36, 37 and 38.

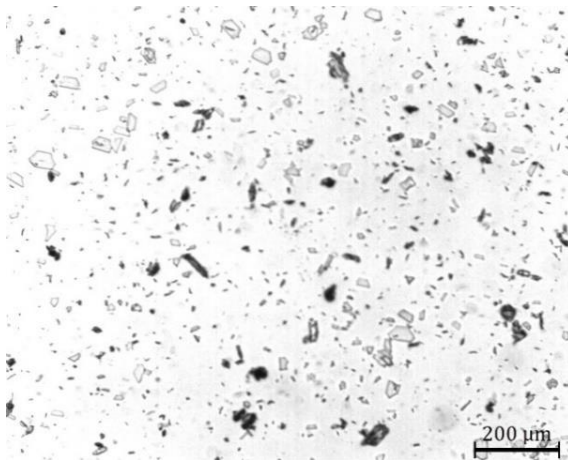


Figure 36 – 0.4% MCC + CTAB

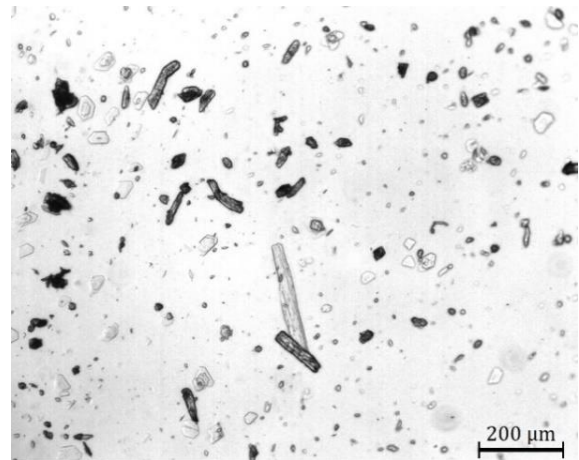


Figure 37 – 1.0% MCC + CTAB

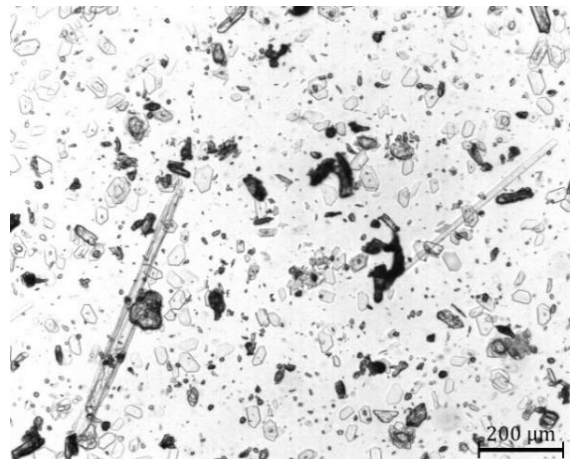


Figure 38 – 1.5% MCC + CTAB

Figure 36 (0.4% MCC) shows very disperse MCC particles. Higher concentrations (1.0% and 1.5% MCC) obtained bigger and more intact MCC particles (less break of the particles). 1.0% MCC have less dispersion than 0.4% and 1.5% MCC.

Phase 2 – 1% MCC + Varying CTAB

The analysis was done using the 3,3x eye piece and the objective at 4x. The results can be viewed in figures 39 to 42.

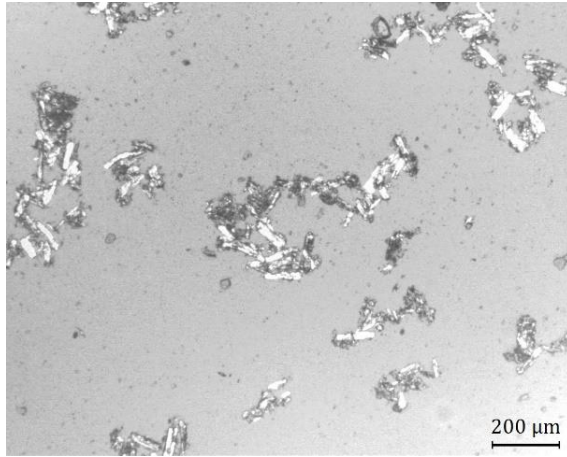


Figure 39 – 1.0% MCC + 40% CTAB

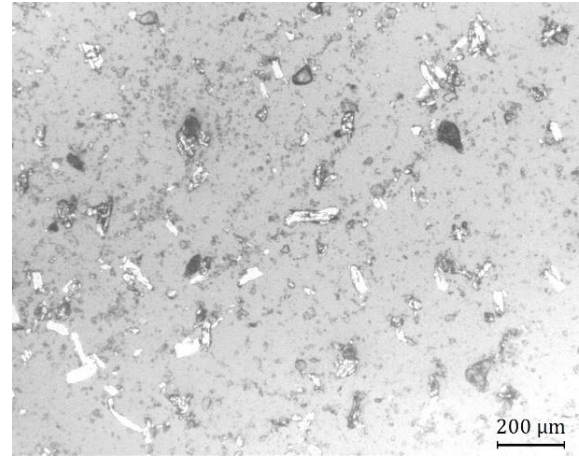


Figure 40 – 1.0% MCC + 60% CTAB

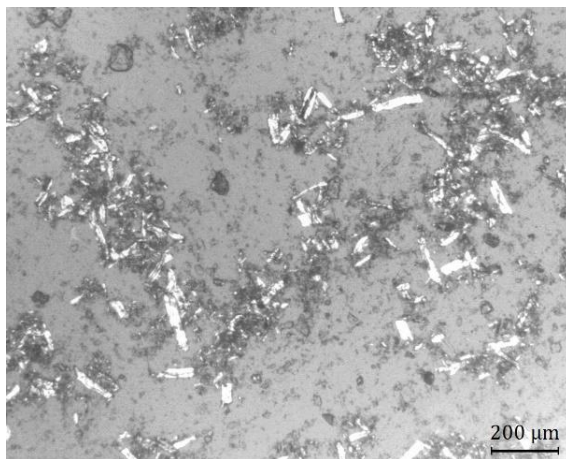


Figure 41 – 1.0% MCC + 80% CTAB

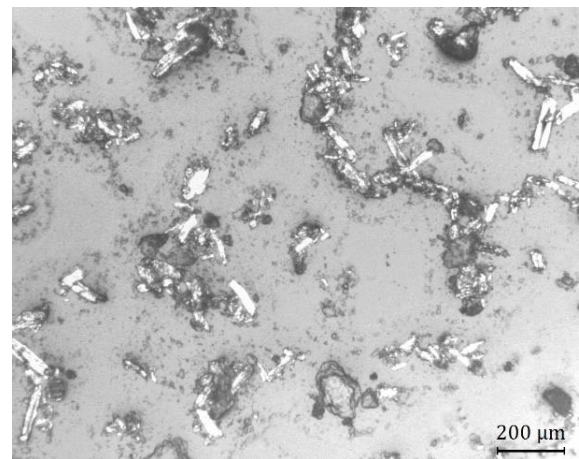


Figure 42 – 1.0% MCC + 100% CTAB

The sample containing 80% CTAB appears to have a higher concentration of MCC, as well as more agglomerations, than the other percentages. The sample with 60% CTAB seems to its particles more evenly dispersed, few agglomerations (Figure 40). 40% CTAB present the least amount of agglomerations.

Phase 3 – Varying MCC + 40% CTAB

The analysis was done using the 3,3x eye piece and the objective at 4x. The results can be viewed in figures 43 and 44.

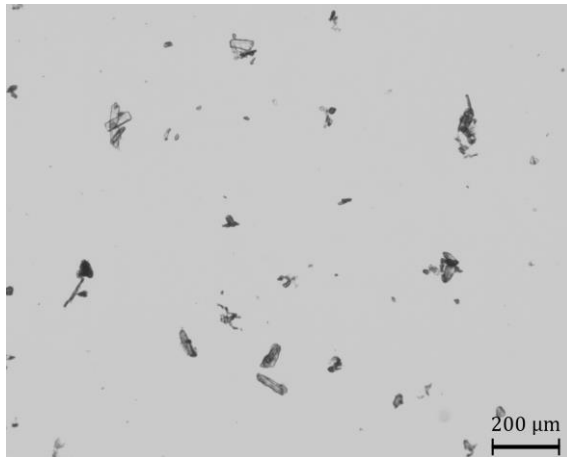


Figure 43 - 0.4% MCC + CTAB

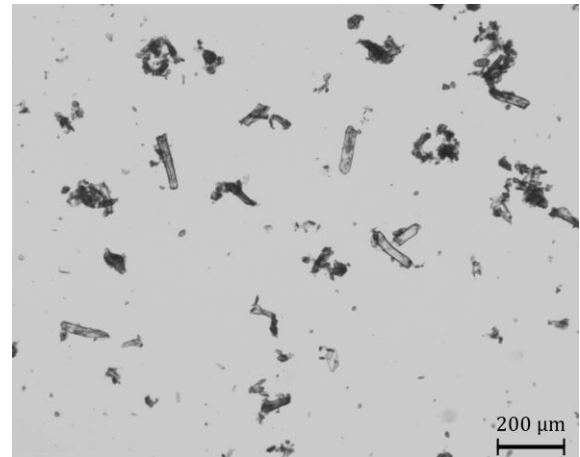


Figure 44 - 1.5% MCC + CTAB

According to the figures the MCC particles appear very disperse, although 1.5% MCC show some agglomerations. The sample with 1.5% MCC has more particles than 0.4%, which is expected.

4.1.4. Sisal Fibres

Using the 1,67x eye piece and the objective at 4x, figures 45 to 47 were obtained.



Figure 45 – Sisal_1

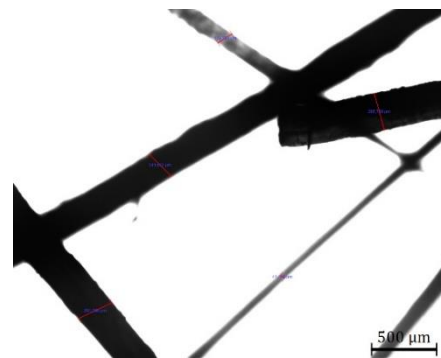


Figure 46 – Sisal_2

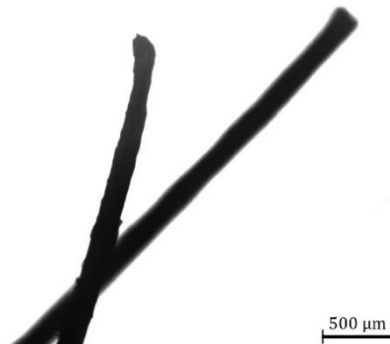


Figure 47 – Sisal_3

Sisal fibres were also characterized by stereoscopic analysis. The eye piece used was 1,67 and the objective was at 2x.

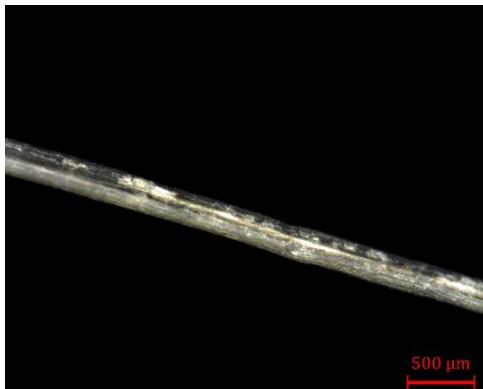


Figure 48 – Sisal_4



Figure 49 – Sisal_5

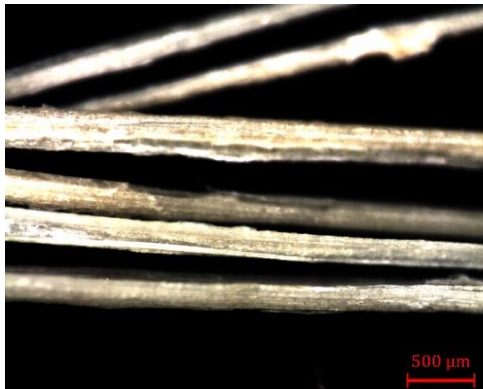


Figure 50 – Sisal_6



Figure 51 – Sisal_7

From the images obtained, it is clear that the thickness of sisal fibres varies greatly which is expected in natural fibres. The surface texture of these fibres vary as some appear smooth while others show irregularities. Through the stereoscopic images (Figures 48, 49, 50 and 51) it can be seen that these fibres are quite fibril.

These variations found in sisal fibres could affect the results when incorporated into the cementitious composite.

4.2. UV Analysis

4.2.1. MCC without Surfactant

The objective of this analysis was learn which percentage of MCC had the best absorption results in water because it is expected that percentage will lead to a more evenly distribution of MCC in the cementitious matrix.

Figure 52 shows the results obtained from the UV analysis of three different percentages of MCC, 0.4%, 1.0% and 1.5%, without surfactant.

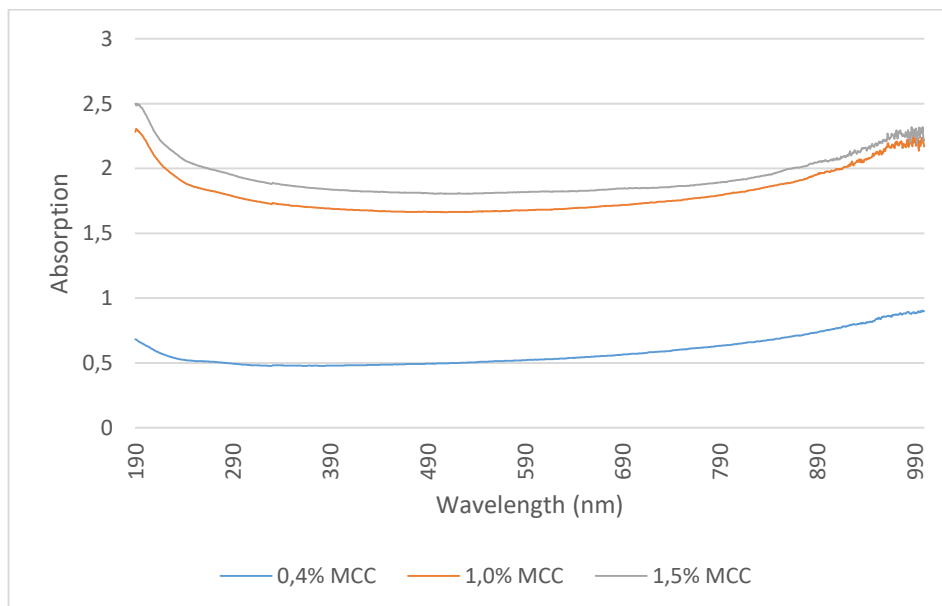


Figure 52 - Spectrum obtained for Varying Percentages of MCC

According to the figure, 0.4% MCC obtained the lowest values for absorption. The percentage of MCC that shows the best results is 1.5%, although 1.0% showed very close results. This was the expected result because as MCC is insoluble in water, the best result would be the sample with the highest percentage.

4.2.2. MCC with Pluronic F-127

The purpose of this analysis was learn which percentage of MCC had the optimal result when used combined with Pluronic F-127. In order to do so three different percentages of MCC,

0.4%, 1.0% and 1.5% w.r.t. water, with 20% of the surfactant Pluronic F127 were analysed. Figure 53 shows the results obtained.

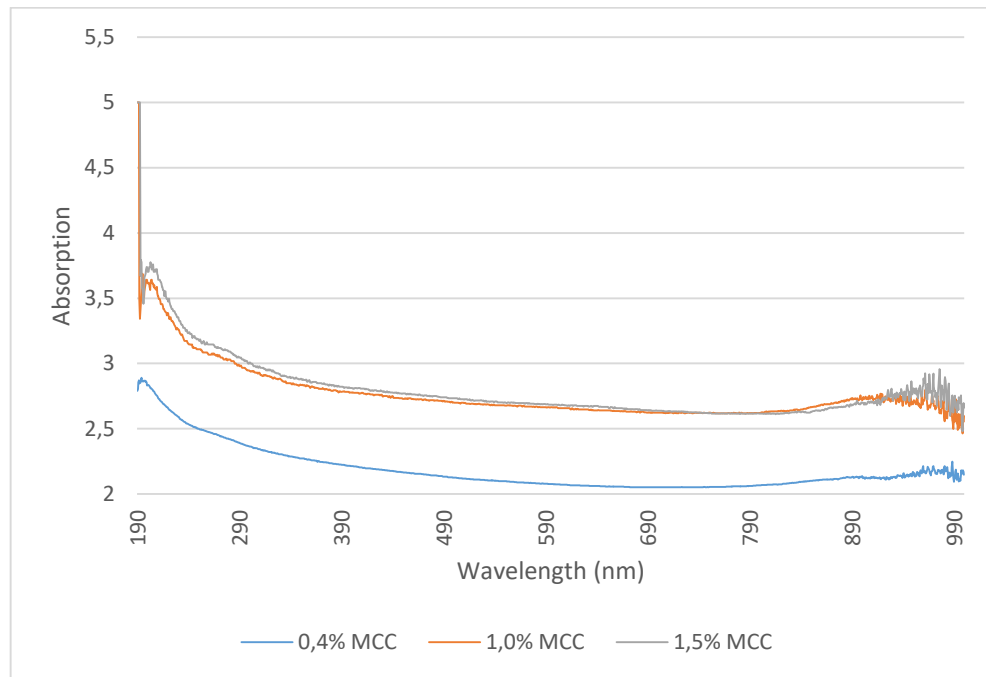


Figure 53 - Spectrum obtained for Varying Percentages of MCC + 20% Pluronic F127

According to Figure 53, 0.4% MCC obtained the lowest absorption values. 1.0% and 1.5% MCC show similar results, which indicates the use of higher percentages than 1.0% MCC is not advantageous. The optimal percentage of MCC for 20% Pluronic F-127 is 1.0%.

4.2.3. MCC with CTAB

In order to evaluate the best percentage of CTAB to add to MCC, four different percentages of CTAB (40%, 60%, 80%, 100%) were analysed with regards to 1.0% of MCC (0.1 g). Figure 54 shows the results obtained from the UV analysis.

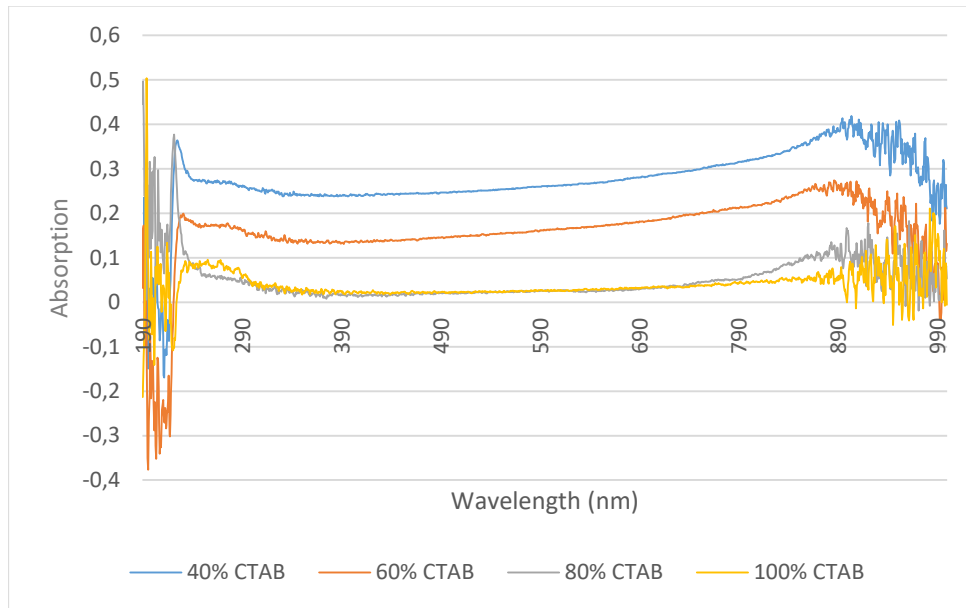


Figure 54 - Spectrum obtained for 1.0% MCC + Varying Percentages of CTAB

Through Figure 54 it can be concluded that the sample with 40% CTAB shows the highest absorption. This being the case, 40% CTAB was then analysed with three different percentages of MCC, 0.4%, 1.0% and 1.5%, in order to obtain the optimal percentage mix of MCC and CTAB. Figure 55 shows the results obtained from the UV analysis.

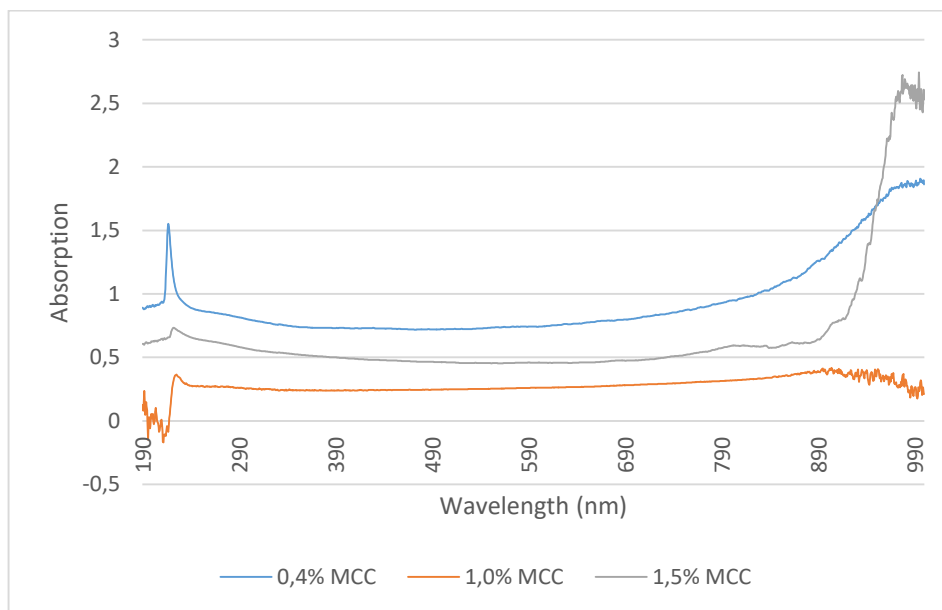


Figure 55 - - Spectrum obtained for Varying Percentages of MCC + 40% CTAB

According to the figure, 0.4% MCC shows the overall best result which means that 0.4% MCC is the optimal percentage to use with 40% of the surfactant CTAB.

4.3. Tensile Behaviour of Sisal Fibres

Tensile strength is the maximum stress that a material can handle before breaking.

Doing an average of the maximum load acquired from the testing of the 50 samples, the average tensile stress attained is 0.325 N/Text. The coefficient of variation obtained was 25%.

The maximum load obtained was 33.60 N with an average of 13.01 N.

The average elongation at break was 4.08% and the maximum elongation at break was 10.90%.

More detailed information on the results obtained for tensile testing of the sisal fibres can be found in Attachment 4.

4.4. Flow Table Test

4.4.1. Cementitious Composites without Surfactant

Table 16 contains the results obtained from the workability test.

Table 16 - Results from workability test (without surfactant)

Sample	Measurement 1	Measurement 2
Plain Mortar	189 mm	187 mm
0.2% MCC + 0.5 ml of SP	168 mm	167 mm
0.5% MCC + 1.0 ml of SP	169 mm	169 mm
0.75% MCC + 0.5 ml of SP	169 mm	174 mm
0.25% Sisal	170 mm	170 mm
0.5% Sisal	169 mm	170 mm
0.25% Sisal + 0.2% MCC	168 mm	168 mm
0.25% Sisal + 0.5% MCC + 1.0 ml of SP	177 mm	181 mm
0.25% Sisal + 0.75% MCC + 0.5 ml of SP	166 mm	165 mm

The inclusion of MCC in the cementitious matrix led to a decrease in the flow parameter, whether it was in the cementitious composites containing only MCC or the ones containing both sisal and MCC. The addition of sisal fibres did not cause any major changes in the workability of the reinforced cementitious matrix.

4.4.2. Cementitious Composites with Pluronic F-127

After well mixed the workability of the mortar was tested, using the same method previously described. Table 17 contains the results from the test.

Table 17 - Results from workability test (with Pluronic F-127)

Sample	Measurement 1	Measurement 2
Plain Mortar	189 mm	187 mm
0.2% MCC + 0.5 ml of SP	198 mm	197 mm
0.5% MCC + 0.5 ml of SP	170 mm	170 mm
0.75% MCC + 0.5 ml of SP	170 mm	169 mm
0.25% Sisal	181 mm	179 mm
0.5% Sisal	172 mm	169 mm
0.25% Sisal + 0.2% MCC	178 mm	171 mm
0.25% Sisal + 0.5% MCC	175 mm	171 mm
0.25% Sisal + 0.75% MCC	172 mm	171 mm

The addition of MCC in the cementitious matrix led to a decrease of workability when used individually but did not affect majorly when added with sisal. Also, the use of Pluronic F-127 seems to have led to an increase in the flow parameter. Again, there were no major changes in the workability when sisal is added to the cementitious matrix.

4.4.3. Cementitious Composites with CTAB

After well mixed the workability of the mortar was tested, using the same method previously described. Tables 18 and 19 contain the results from the workability test using 40% and 100% CTAB, respectively.

Table 18 - Results from workability test (with 40% CTAB)

Sample	Measurement 1	Measurement 2
Plain Mortar	189 mm	187 mm
0.2% MCC	188 mm	189 mm
0.5% MCC	167 mm	166 mm
0.75% MCC	185 mm	190 mm
0.25% Sisal	181 mm	186 mm
0.5% Sisal	192 mm	188 mm
0.25% Sisal + 0.2% MCC	174 mm	173 mm
0.25% Sisal + 0.5% MCC	178 mm	182 mm
0.25% Sisal + 0.75% MCC	172 mm	177 mm

Table 19 - Results from workability test (with 100% CTAB)

Sample	Measurement 1	Measurement 2
Plain Mortar	189 mm	187 mm
0.25% Sisal + 0.2% MCC	169 mm	170 mm
0.25% Sisal + 0.5% MCC	183 mm	187 mm

The use of CTAB appears to have led to an increase in the flow parameter, which means the use of superplasticizer was not required in any of the cementitious composites.

The composites containing MCC, for the most part have increased but curiously the one with 0.5% MCC did not increase as greatly when compared to lower and higher percentages (0.2% and 0.75% MCC w.r.t. cement).

4.5. Flexural Strength Testing

4.5.1. Cementitious Composites Reinforced without Surfactant

Figure 56 and Table 20 contain the results of the flexural strength testing of the samples made without use of surfactant.

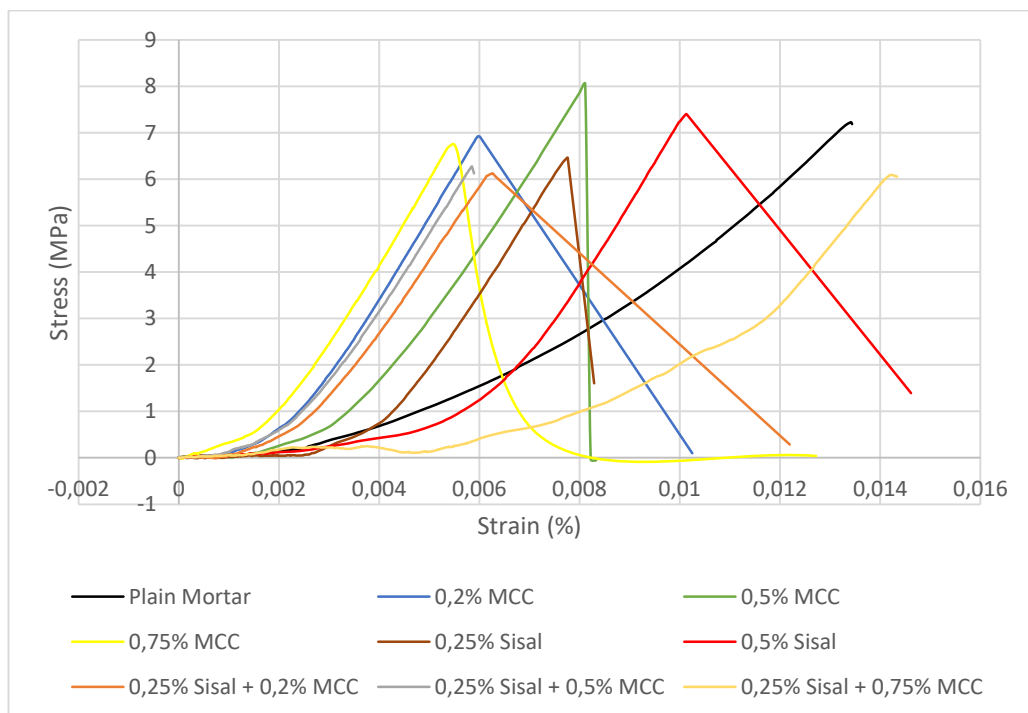


Figure 56 - Flexural strength of reinforced mortar without surfactant

Table 20 - Flexural strength of reinforced mortar without surfactant

Sample	Maximum Load (N)	Maximum Stress (MPa)	% Improv.	Strain (%)
Plain Mortar	3082.66	7.22	0.00	0.0134
0.2% MCC	2953.19	6.92	-4.20	0.0060
0.5% MCC	3432.27	8.04	11.34	0.0081
0.75% MCC	2883.17	6.76	-6.47	0.0055
0.25% Sisal	2754.96	6.46	-10.63	0.0078
0.5% Sisal	3156.02	7.40	2.38	0.0101
0.25% Sisal + 0.2% MCC	2611.53	6.12	-15.28	0.0063
0.25% Sisal + 0.5% MCC	2677.03	6.27	-13.16	0.0059
0.25% Sisal + 0.75% MCC	2598.54	6.09	-15.70	0.0142

The figure clearly shows that the sample containing 0.5% MCC obtained the highest flexural stress (8.04 MPa). The addition of MCC in the cementitious composites has led to an increase of stiffness.

0.5% sisal also obtained a good stress result when compared with the plain mortar. The addition of sisal fibres achieved higher ductility of the cementitious matrix when compared with MCC reinforced cementitious composites. Moreover, it is enhancing the post peak load bearing capacity of cementitious matrix.

The cementitious composite reinforced with 0.25% sisal and 0.75% MCC w.r.t. cement (multiscale cementitious composite) resulted in a highly ductile cementitious composite with a similar curve to the plain cement mortar (reference sample) but with lower strength values.

4.5.2. Cementitious Composites Reinforced with Pluronic F-127

Figure 57 and Table 21 contain the results obtained for flexural strength of the samples made using the surfactant Pluronic F-127.

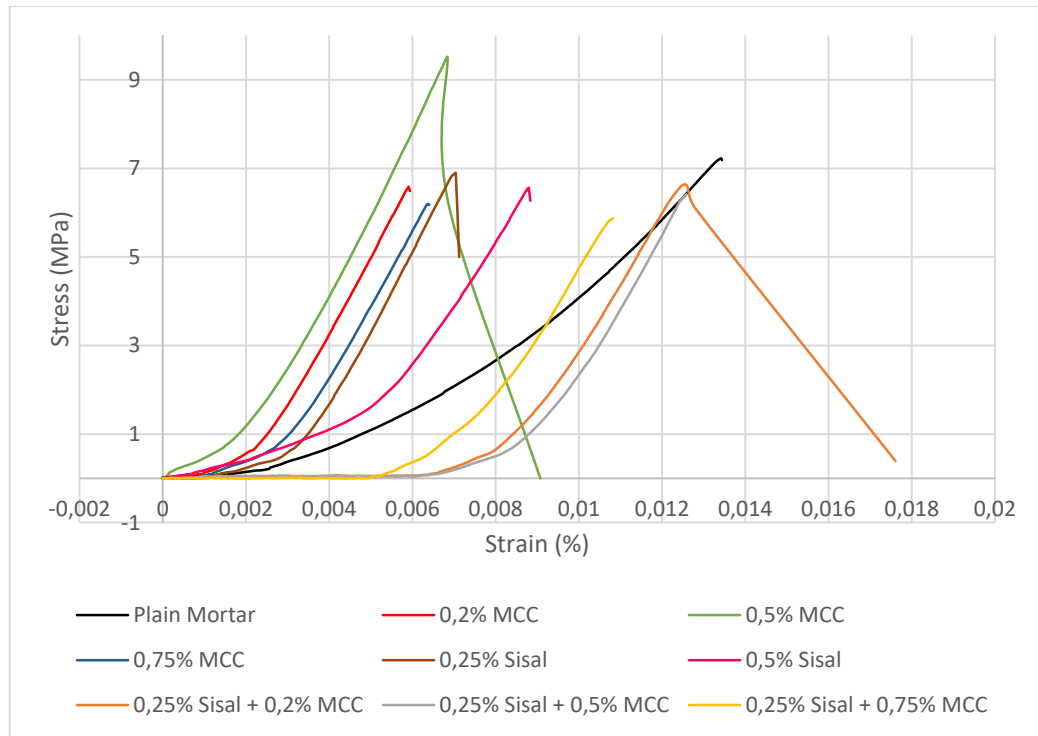


Figure 57 - Flexural strength of reinforced mortar with Pluronic F127

Table 21 - Flexural strength of reinforced mortar with Pluronic F127

Sample	Maximum Load (N)	Maximum Stress (MPa)	% Improv.	Strain (%)
Plain Mortar	3082.66	7.22	0.00	0.0134
0.2% MCC	2809.26	6.58	-8.87	0.0059
0.5% MCC	4061.87	9.52	31.74	0.0068
0.75% MCC	2644.53	6.20	-14.21	0.0064
0.25% Sisal	2942.68	6.90	-4.54	0.0070
0.5% Sisal	2799.36	6.56	-9.19	0.0088
0.25% Sisal + 0.2% MCC	2832.35	6.64	-8.12	0.0126
0.25% Sisal + 0.5% MCC	2735.79	6.41	-11.25	0.0126
0.25% Sisal + 0.75% MCC	2505.19	5.87	-18.73	0.0108

Stiffness has increased with the addition of MCC in all MCC reinforced cementitious composites. 0.5% MCC has the highest stress with 9.52 MPa.

Again, the cementitious composites with sisal fibres have higher ductility than MCC reinforced cementitious composites.

4.5.3. Cementitious Composites Reinforced with 100% CTAB

Figure 58 and Table 22 display the results for flexural strength for the samples made using the 100% of the surfactant CTAB.

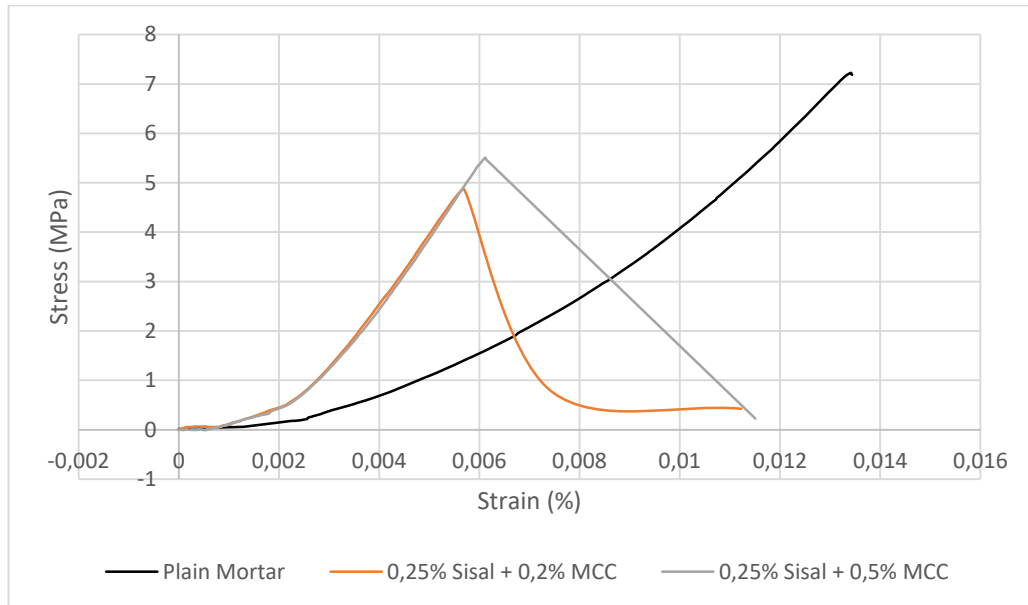


Figure 58 - Flexural strength of reinforced mortar with 100% CTAB

Table 22 - Flexural strength of reinforced mortar with 100% CTAB

Sample	Maximum Load (N)	Maximum Stress (MPa)	% Improv.	Strain (%)
Plain Mortar	3082.66	7.22	0.00	0.0134
0.25% Sisal + 0.2% MCC	2078.33	4.87	-32.58	0.0057
0.25% Sisal + 0.5% MCC	2349.74	5.51	-23.78	0.0061

The results for flexural strength obtained for the samples made using 100% CTAB are significantly lower than the results for the plain mortar. There is a significant increase of stiffness and therefore an increase in the flexural modulus.

Due to the low results, the next samples studied contained 40% CTAB (percentage that showed the best absorption in the UV testing of MCC).

4.5.4. Cementitious Composites Reinforced with 40% CTAB

Figure 59 and Table 23 show the results for flexural strength for the samples made using the 40% of the surfactant CTAB.

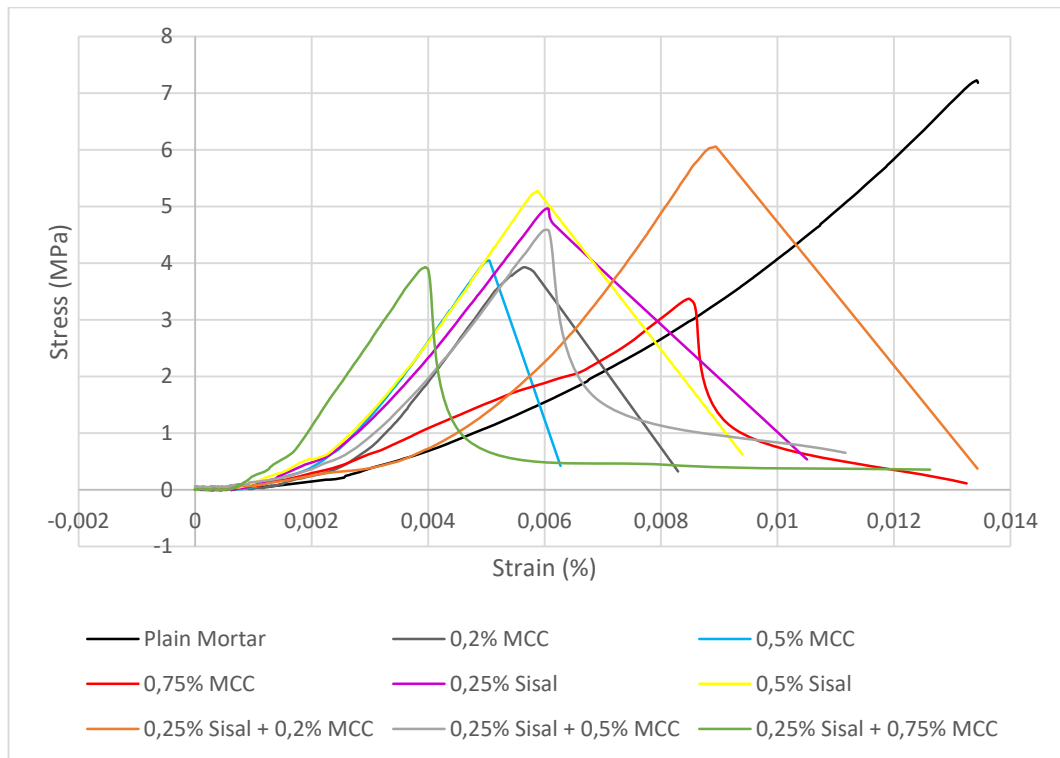


Figure 59 - Flexural strength of reinforced mortar with 40% CTAB

Table 23 - Flexural strength of reinforced mortar with 40% CTAB

Sample	Maximum Load (N)	Maximum Stress (MPa)	% Improv.	Strain (%)
Plain Mortar	3082.66	7.22	0.00	0.0134
0.2% MCC	1675.54	3.93	-45.65	0.0056
0.5% MCC	1723.71	4.04	-44.08	0.0050
0.75% MCC	1436.60	3.37	-53.40	0.0085
0.25% Sisal	2116.95	4.96	-31.33	0.0060
0.5% Sisal	2251.39	5.28	-26.97	0,0059
0.25% Sisal + 0.2% MCC	2580.96	6.05	-16.27	0,0090
0.25% Sisal + 0.5% MCC	1957.74	4.59	-36.49	0,0060
0.25% Sisal + 0.75% MCC	1675.81	3.93	-45.64	0.0040

The flexural strength results obtained for the samples containing 40% CTAB are all lower than the result obtained for the plain mortar, but higher than the results obtained for 100% CTAB. As the samples containing 40% CTAB show slightly better results, the problem could be the incorrect use of CTAB. Further study should be made on the use of the surfactant CTAB with cementitious composites.

The cementitious composite with 0.25% sisal and 0.2% MCC obtained the highest stress value with 6.05 MPa, followed by the cementitious composites with 0.25% and 0.5% sisal fibres (obtaining 4.96 MPa and 5.28 MPa, respectively). 0.75% MCC obtained the lowest stress value with 3.37 MPa.

In Figure 59, it can be seen that the cementitious composites reinforced with MCC and sisal fibres show an increase of stiffness with the increase of the percentage of MCC.

4.5.5. Fracture Energy

Fracture energy (G_F) is an important material property that helps describe the fracture characteristics of concrete. The parameter G_F is defined as the energy absorbed to create a unit area of fracture surface. The fracture energy was determined with the use of the software Origin Pro and the flexural curve (Machine extension/Load).

Tables 24 to 27 contain the fracture energy of the samples tested as well as the percentage improvement obtained when compared with the plain cement mortar.

Table 24 – Fracture energy results (without surfactant)

Sample	Fracture Energy (N/mm)	% Improvement
Plain Mortar	804.3	0.00
0.2% MCC	522.1	-35.09
0.5% MCC	380.2	-52.73
0.75% MCC	384.6	-52.18
0.25% Sisal	277.9	-65.45
0.5% Sisal	682.9	-15.09
0.25% Sisal + 0.2% MCC	571.4	-28.96
0.25% Sisal + 0.5% MCC	227.7	-71.69
0.25% Sisal + 0.75% MCC	382.9	-52.39

Table 25 – Fracture energy results (with Pluronic F-127)

Sample	Fracture Energy (N/mm)	% Improvement
Plain Mortar	804.3	0.00
0.2% MCC	586.7	-27.06
0.5% MCC	449.7	-44.09
0.75% MCC	395.7	-50.80
0.25% Sisal	742.6	-7.67
0.5% Sisal	620.1	-22.91
0.25% Sisal + 0.2% MCC	634.7	-21.09
0.25% Sisal + 0.5% MCC	256.1	-68.16
0.25% Sisal + 0.75% MCC	232.4	-71.11

Table 26 – Fracture energy results (with 40% CTAB)

Sample	Fracture Energy (N/mm)	% Improvement
Plain Mortar	804.3	0.00
0.2% MCC	224.8	-72.05
0.5% MCC	163.8	-79.64
0.75% MCC	265.0	-67.05
0.25% Sisal	395.1	-50.88
0.5% Sisal	374.2	-53.48
0.25% Sisal + 0.2% MCC	542.4	-32.57
0.25% Sisal + 0.5% MCC	293.9	-63.46
0.25% Sisal + 0.75% MCC	204.9	-74.53

Table 27 – Fracture energy results (with 100% CTAB)

Sample	Fracture Energy (N/mm)	% Improvement
Plain Mortar	804.3	0.00
0.25% Sisal + 0.2% MCC	293.8	-63.47
0.25% Sisal + 0.5% MCC	474.7	-40.98

The cementitious composites reinforced with 0.2% MCC w.r.t. cement, with Pluronic F-127 and without surfactant, showed the best fracture energy values of the MCC incorporated composites.

With regards to the cementitious composites reinforced with sisal, 0.25% had slightly higher fracture energy than 0.5% when using surfactant (Pluronic F-127 or CTAB), while 0.5% had a higher result than 0.25% (by a big margin) when no surfactant was used.

The percentage combination 0.25% sisal and 0.2% MCC w.r.t. cement had the overall best fracture energy results when compared with the other multiscale reinforced cementitious

composites studied throughout this work. The cementitious composites using 100% CTAB were the exception, as 0.25% sisal and 0.5% MCC w.r.t. cement had the best result, in this case.

The fracture energy of optimized sisal reinforced cementitious composites showed slightly lower values than the plain cement mortar in 28 days of hydration.

4.6. Compressive Strength Testing

Figure 60 and Table 28 show the results from the compressive strength testing.

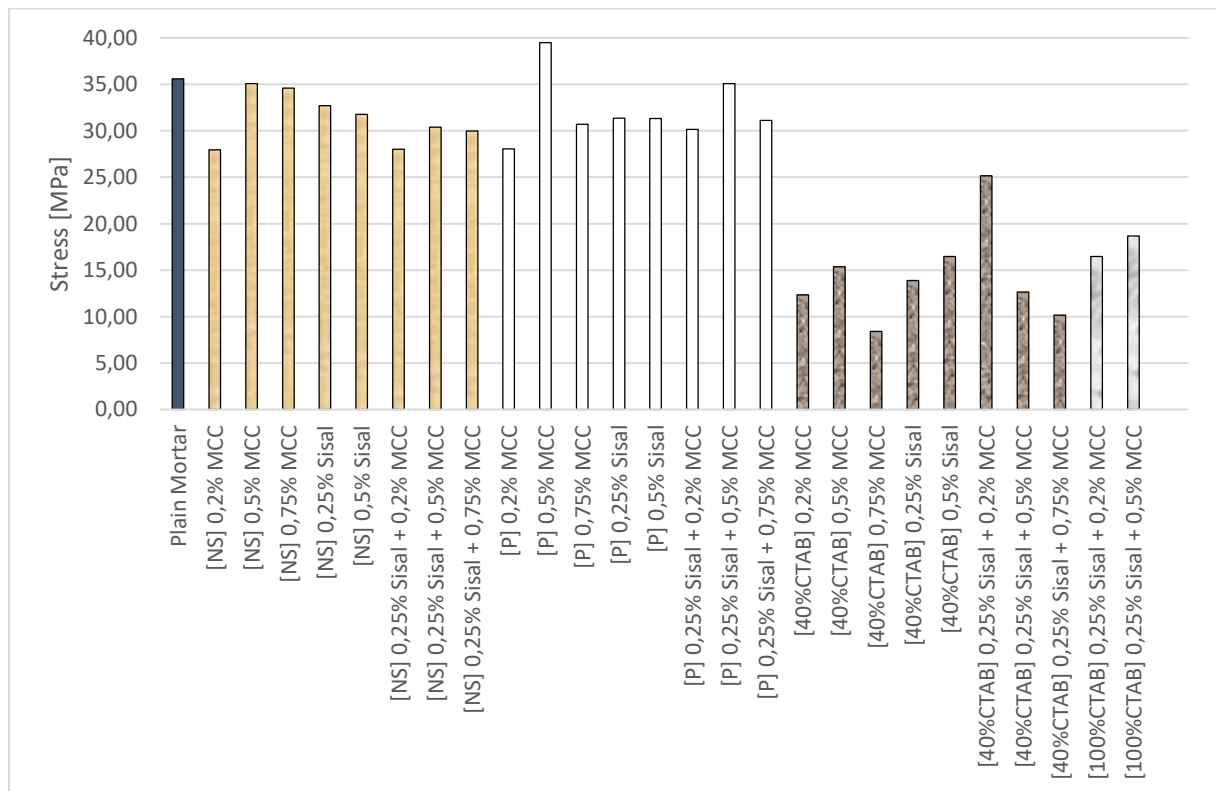


Figure 60 - Compressive strength results

From the results obtained in the figure, it can be concluded that 0.5% MCC works better than higher percentages, as it has the best compressive strength results regardless of the use or not of surfactant.

The results clearly show that there was no improvement in the compressive strength testing, with the exception of the cementitious composite reinforced with 0.5% MCC w.r.t. cement (20% Pluronic F127 w.r.t. MCC) which showed improvement (10.96 %).

The choice of surfactant also affected the results seeing as the samples containing CTAB obtained the worst results. The combination of 0.25% sisal and 0.2% MCC obtained the best result with 25.16 MPa but it was still lower than any of the results obtained for the cementitious composites with Pluronic F-127 and without surfactant.

Table 28 - Compressive strength results

Sample		Stress (MPa)	% Improv.	% CV
Plain Mortar		35.60	0.00	13.2
No Surfactant	0.2% MCC	27.94	-21.52	5.0
	0.5% MCC	35.06	-1.52	2.7
	0.75% MCC	34.61	-2.78	3.2
	0.25% Sisal	32.71	-8.12	4.5
	0.5% Sisal	31.78	-10.73	5.8
	0.25% Sisal + 0.2% MCC	28.02	-21.29	6.0
	0.25% Sisal + 0.5% MCC	30.40	-14.61	8.7
	0.25% Sisal + 0.75% MCC	29.99	-15.76	10.7
20% Pluronic F127	0.2% MCC	28.03	-21.26	7.7
	0.5% MCC	39.50	10.96	2.7
	0.75% MCC	30.70	-13.76	5.2
	0.25% Sisal	31.37	-11.88	5.8
	0.5% Sisal	31.33	-11.99	6.1
	0.25% Sisal + 0.2% MCC	30.14	-15.34	9.8
	0.25% Sisal + 0.5% MCC	35.06	-1.52	11.6
	0.25% Sisal + 0.75% MCC	31.13	-12.56	7.4
40% CTAB	0.2% MCC	12.33	-65.37	7.2
	0.5% MCC	15.36	-56.85	4.9
	0.75% MCC	8.39	-76.43	11.8
	0.25% Sisal	13.88	-61.01	9.9
	0.5% Sisal	16.48	-53.71	6.9
	0.25% Sisal + 0.2% MCC	25.16	-29.33	4.3
	0.25% Sisal + 0.5% MCC	12.65	-64.47	3.6
	0.25% Sisal + 0.75% MCC	10.18	-71.40	10.7
100% CTAB	0.25% Sisal + 0.2% MCC	16.46	-53.76	11.6
	0.25% Sisal + 0.5% MCC	18.68	-47.53	7.3

All the samples tested obtained relatively low coefficients of variation which is good as it means the results are very similar and therefore more accurate.

Chapter 5 - CONCLUSION

This thesis reports the work on multiscale cementitious composite reinforced with microcrystalline cellulose and sisal fibres. The main goal of this work is to optimize a feasible process to incorporate sisal fibres and MCC in cementitious matrix and also to analyse the mechanical behaviour of multiscale cementitious composites. To achieve proper dispersion of microcrystalline cellulose, two different kinds of surfactants were used along with sonication energy. Sisal fibres (20 mm) are mixed manually in cement before the mixing process.

1. UV-Vis spectroscopy has been done to characterize the stability of MCC (0.4%, 1% and 1.5% w.r.t. water) in water. This was achieved through three processes, using cationic surfactant (CTAB), non-ionic surfactant (Pluronic F-127) and with no surfactant, the best results were obtained by non-ionic surfactant.
2. The stable suspension of MCC in water was obtained by using surfactant and/or ultrasonication energy. The obtained stable suspension was utilized to reinforce the cementitious matrix. Multiscale cementitious composites were developed by using stable mcc suspension and sisal fibres.
3. Flexural strength testing indicates that 0.5% of sisal fibres increased the flexural strength of cementitious composites by 2.38% in the cementitious composite that contained no surfactant. In addition, 0.5% of MCC increased the flexural strength of cementitious composites by 31.74% in the cementitious composite containing 20% Pluronic F127 and by 11.34% in the one that contained no surfactant.
4. The stiffness (flexural modulus) of cementitious matrix was increased by the addition of MCC. This can be explained due to crystalline nature and high stiffness of MCC.

5. MCC and sisal fibres reinforced cementitious composites showed improvement in pre peak as well as post peak mechanical behaviour respectively. Since it is the first reported work on multiscale cementitious composite, in future more focus should be on optimizing the dispersion route as well as influence of MCC on hydration of cementitious matrix.
6. The flexural strength did not improve on incorporation of MCC and sisal fibres due to hygroscopic nature of MCC and sisal fibres. In detail study is required to analyse the hydration effect of these fibres on cementitious matrix. Different hydration days (42 days and 56 days) samples of reinforced cementitious matrix should be studied to analyse the increase of flexural strength with time.
7. There is no significant change in compressive strength after incorporation of sisal fibres and mcc together in cementitious matrix. 0.5% MCC in cementitious matrix (containing the surfactant Pluronic F127) showed the best result with 10.96% improvement over the plain cementitious mortar.
8. The cementitious composites containing CTAB have lower density than plain mortar sample. The cementitious composites containing Pluronic F127 have slightly higher densities. Samples not containing surfactant have similar values of density when compared with plain mortar sample. The densities can be observed in Attachment 7.

5.1. Future Work

This research work can definitely be developed further. The use of MCC and natural fibres as reinforcing elements for cementitious composites can bring great advantages to civil engineering industry and should be the target of additional study. In specific, this dissertation can lead to other exploratory works, such as:

1. Different cement/water ratios should be studied for cementitious composites reinforced with MCC and sisal fibres.
2. Cementitious composites reinforced with MCC and other natural fibres should be studied.
3. Reinforcement of the cementitious matrix with nanocelulose and natural fibres could be an interesting subject to analyse.
4. Further study should be done on the combined use of the surfactant CTAB and MCC. Different percentage combinations could lead to an improvement of the cementitious composites characteristics and properties.
5. The hydration effect of MCC and sisal fibres when incorporated in the cementitious matrix should be further analysed using different hydration days (42 days and 56 days, for example), in order to determine if there is an increase of flexural strength with time.

BIBLIOGRAPHY

- Adel, A., El-Wahab, Z., Ibrahim, A., Al-Shemy, M. (2011) Characterization of microcrystalline cellulose prepared from lignocellulosic materials, *Part II: Physicochemical properties*, *Carbohydrate Polymers*, 83, 676–687
- Agopyan, V., Savastano, H., John, V., Cincotto, M. (2005) Developments on vegetable fibre–cement based materials in São Paulo, Brazil: an overview, *Cement & Concrete Composites* 27, 527–536
- Arboleda, D. (2014) Fabric Reinforced Cementitious Matrix (FRCM) Composites for Infrastructure Strengthening and Rehabilitation: Characterization Methods, available at: http://scholarlyrepository.miami.edu/oa_dissertations
- Avicel (2008) Material Safety Data Sheet: Avicel® PH Microcrystalline Cellulose, *FMC BioPolymer*, available at: <http://www.fmcbiopolymer.com/portals/pharm/content/docs/avicelphmsds.pdf>, consulted on August 13th
- Bentur, A., Mindess, S. (2007) Introduction, *Fibre Reinforced Cementitious Composites, Second Edition*
- BS EN 1015-03:2004 - (2004) – “*Determination of consistence of fresh mortar (by flow table)*” – European Standard.
- BS EN 1015-11:1999 (1999) – “*Determination of flexural and compressive strength of hardened mortar*” – European Standard
- Carmona-Ribeiro, A., Carrasco, L. (2013) Cationic Antimicrobial Polymers and Their Assemblies, *International Journal of Molecular Science*, 14(5), 9906-9946
- Gonzalez, J. (2007) Betões Reforçados com Fibras de Carbono Estudo de Propriedades Mecânicas e Físicas, *Tese de Doutorado Engenharia Civil, Universidade do Minho*
- Hoyos, C., Cristia, E., Vázquez, A. (2013) Effect of cellulose microcrystalline particles on properties of cement based composites, *Materials and Design*, 51, 810–818.

Kim, M., Park, Y., Okoli, O., Zhang, C. (2009) Processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites, *Composites Science and Technology* 69, 335–342

Klerk M. (2015) The Durability of Natural Sisal Fibre Reinforced Cement-based Composites, Thesis presented in fulfilment of the requirements for the degree of Master in Engineering in the Faculty of Engineering at Stellenbosch University, available at: <http://scholar.sun.ac.za/handle/10019.1/96895?show=full>, consulted on March 24th

Li, Z., Wang, X., Wang, L. (2006) Properties of hemp fibre reinforced concrete composites, *Composites Part A*, 37, 497–505.

Menou, A., Mounajed, G., Boussa, H., Pineaud, A., Carre, H. (2006) Residual fracture energy of cement paste, mortar and concrete subject to high temperature, *Theoretical and Applied Fracture Mechanics*, 45, 64–71

Mohammed, M., Ahmed, A., Osman, R. (2014) Microcrystalline cellulose as a reinforcement agent to cement pastes, *Pigment & Resin Technology*, 43, 104–110.

Onuaguluchi, O., Banthia, N. (2016) Plant-based natural fibre reinforced cement composites: A review, *Cement and Concrete Composites* 68, 96-108.

P.V. Joseph, Kuruvilla, J., Sabu, T. (1999) Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites, *Composites Science and Technology*, 59, 1625±1640

Pakravan, H., Jamshidi, M., Latifi, M., Torgal, F. (2011) Cementitious Composites Reinforced With Polypropylene, Nylon and Polyacrylonitile Fibres

Premix (2016) Why Composites?, *Engineering, Compounding and Moulding of Thermoset Composites*, available at: <http://www.premix.com/why-composites/adv-composites.php>, consulted on October 1st

Ramakrishna, G., Sundararajan, T. (2005) Impact strength of a few natural fibre reinforced cement mortar slabs: a comparative study, *Cement & Concrete Composites*, 27, 547–553.

S. Thomas, L. A. Pothan (2008) Natural Fibre Composites – State of the Art, New Challenges and Opportunities, *Natural Fibre Reinforced Polymer Composites: From Macro to Nanoscale*, 3-13.

SECIL (2004) Cimento Portland de Calcário CEM II/A-L 42,5R, available at: <http://www.secil.pt/pdf/CEMIIAL425R.pdf>, consulted on October 1st

Silva, J., Rodrigues, D. (2007) Compressive strength of low resistance concrete manufactured with sisal fiber, *Salvador, Brazil: Brazilian Congress of Ceramics*, 51.

SOCIETE NOUVELLE DU LITTORAL (2016) CEN STANDARD SAND, available at: http://www.s-n-l.fr/iso_album/fiches-produits/10%20Sable%20EN%20196-1/10-Sand-EN-196-1-english-1011.pdf, consulted on October 1st

Swamy, R. (1990) Vegetable fibre reinforced cement composites – a false dream or a potential reality?, *Proceedings of the 2nd international symposium on vegetable plants and their fibres as building materials, Rilem Proceedings 7, Chaman and Hall*; 3–8.

Swift, D., Smith, R. (1979) The flexural strength of cement-based composites using low modulus (sisal) fibres, *Composites, Volume 10, Issue 3*, 145-148.

Torgal, F., Jalali, S. (2011) Cementitious building materials reinforced with vegetable fibres: A review, *Construction and Building Materials 25*, 575–581.

ATTACHMENT 1 - CHARACTERISTICS OF THE CEMENT

(SECIL, 2004)

Portland Limestone-Cement

CEM II / A-L 42,5 R

TABLE A1.1 - CHEMICAL CHARACTERISTICS

Properties	Testing Method	Specific Value w.r.t. cement bulk
Sulphate Content (in SO ₃)	NP EN 196-2	≤ 4.0 %
Chloride Content	NP EN 196-21	≤ 0.10 %

TABLE A1.2 - MECHANICAL CHARACTERISTICS

Compressive Strength (MPa) - NP EN 196-1		
2 days	7 days	28 days (Reference)
≥ 20	-	≥ 42.5 and ≤ 62.5

TABLE A1.3 - PHYSICAL CHARACTERISTICS

Properties	Testing Method	Specific Value
Initial Setting Time	NP EN 196-3	≥ 60 min
Expansibility	NP EN 196-3	≤ 10 min

The following graph contains the average values of compressive strength of concrete made with 350 kg/m³ of cement CEM II / A-L 42,5 R

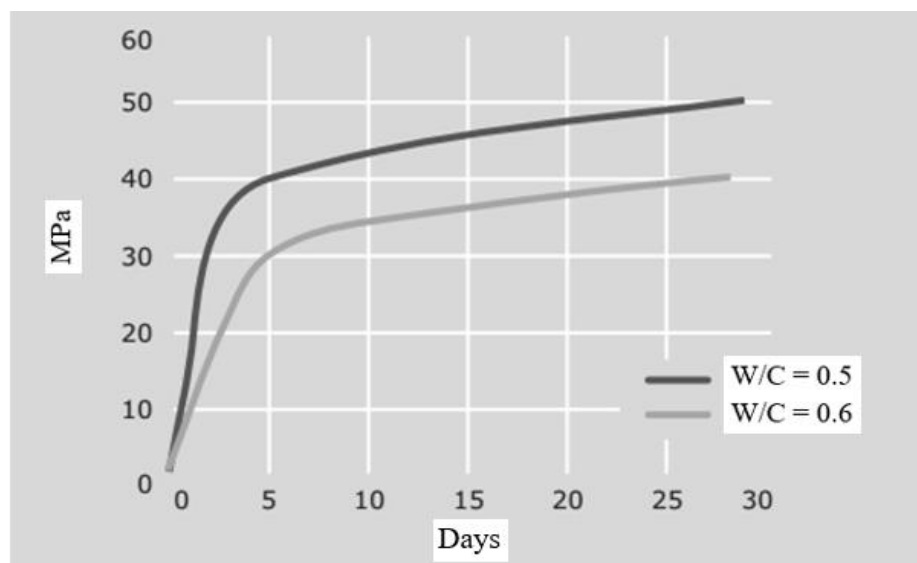


FIGURE A1.1 - COMPRESSIVE STRENGTH OF CONCRETE

ATTACHMENT 2 - CHARACTERISTICS OF THE STANDARD SAND

(SOCIETE NOUVELLE DU LITTORAL, 2016)

CEN Standard Sand

Certified in accordance with EN 196-1 conforming to ISO 679

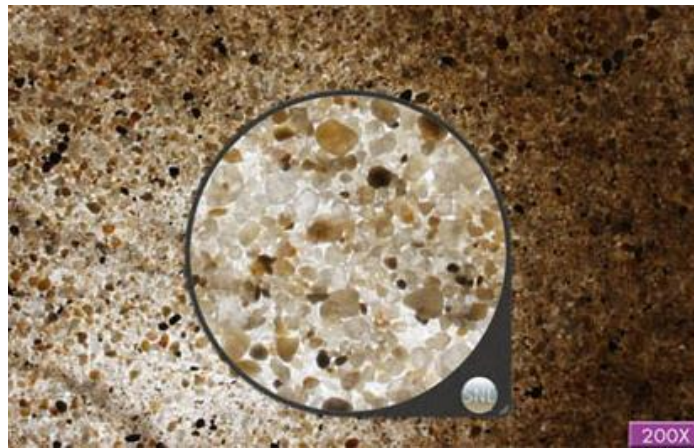


FIGURE A2.1 – IMAGE OF STANDARD SAND

The grading, measured by sieving, complies with the requirements of EN 196-1 and of ISO 679: 2009.

TABLE A2.1 – GRADING RESULTS

Square mesh size (mm)	Cumulative (%) retained
0.08	99 ± 1
0.16	87 ± 5
0.50	67 ± 5
1.00	33 ± 5
1.60	7 ± 5
2.00	0

This analysis is complemented by bag mass controls, water content controls and strength controls, in accordance with EN 196-1 and ISO 679: 2009.

CEN standard conformity is carried out by L.E.M.V.P. (Material Test Laboratory)

ATTACHMENT 3 - CHARACTERISTICS OF THE MCC USED

(Avicel®, 2008)

Avicel® PH Microcrystalline Cellulose

CHEMICAL FAMILY: Carbohydrate

SYNONYMS: Microcrystalline cellulose (INCI name): MCC, cellulose gel

ALTERNATE PRODUCT NAME(S): Avicel PH 101, 102, 103, 105, 112, 200, 113, 301, 302, 200LM

TABLE A3.1 - PHYSICAL AND CHEMICAL PROPERTIES

Odour	Odourless
Appearance	White, free-flowing powder
Auto ignition temperature	Not applicable
Boiling Point	Not applicable
Coefficient of oil / water	(Kow) Not applicable
Evaporation rate	(Butyl acetate = 1) Not applicable
Flash point	Not applicable
Melting point	Not applicable
Oxidizing properties	Not applicable
Percent volatile	Typically 1 – 5 % water, by weight
pH	(In solution) 5.0 – 7.0 (11% solids dispersion)
Solubility in water	(% by weight) Insoluble
Specific gravity	(H ₂ O = 1) Bulk density, 0.2 – 0.5 g/cc
Vapour density	(Air = 1) Not applicable
Vapour pressure	Not applicable

COMMENTS

Explosive Properties of Microcrystalline cellulose: St-1

Minimum Ignition Temperature of Microcrystalline cellulose: 420°C

DISPOSAL CONSIDERATIONS

Disposal Method: No special disposal methods are suggested. It is the user's responsibility to comply with all applicable local, state, and federal laws, rules, regulations and standards.

ATTACHMENT 4 – TENSILE BEHAVIOUR OF SISAL FIBRES

RESULTS

TABLE A4.1 – TENSILE TESTING OF SISAL FIBRES

Samples	Weight [g]	Linear Mass [Tex]	Maximum Strength [N]	Maximum Elongation [%]	Tensile Stress [N/Tex]
1	0.0064	6.40	8.50	10.590	0.2643
2	0.0057	2.85	8.75	2.920	0.3085
3	0.0056	1.87	7.58	3.220	0.2705
4	0.0053	1.33	5.83	2.880	0.2204
5	0.0053	1.06	7.58	3.240	0.2866
6	0.0042	20.95	5.08	8.260	0.2422
7	0.0053	26.50	5.93	3.032	0.2236
8	0.0046	0.58	13.00	3.308	0.5680
9	0.0129	1.43	20.00	2.940	0.3101
10	0.0128	1.28	14.08	7.300	0.2199
11	0.0133	1.21	17.43	10.900	0.2632
12	0.0132	1.10	23.68	3.288	0.3587
13	0.0077	0.59	14.33	2.760	0.3721
14	0.0076	0.54	10.33	5.130	0.2724
15	0.0070	0.47	14.00	2.648	0.4000
16	0.0081	0.51	12.08	4.200	0.2989
17	0.0085	0.50	14.08	2.360	0.3320
18	0.0080	0.44	15.43	3.080	0.3856
19	0.0105	0.55	12.93	7.540	0.2448
20	0.0049	0.25	6.43	2.050	0.2622
21	0.0043	0.20	5.33	5.630	0.2483
22	0.0045	0.20	6.25	3.528	0.2778
23	0.0064	0.28	13.75	3.088	0.4318
24	0.0075	0.31	14.75	3.420	0.3943
25	0.0068	0.27	12.93	2.920	0.3810
26	0.0076	0.29	15.93	3.580	0.4191
27	0.0135	0.50	23.93	2.680	0.3555
28	0.0061	0.22	10.25	2.764	0.3377
29	0.0055	0.19	10.33	3.810	0.3764
30	0.0135	0.45	33.60	3.488	0.4993
31	0.0077	0.25	10.93	4.410	0.2839
32	0.0045	0.14	5.83	7.100	0.2589
33	0.0151	0.46	18.08	8.740	0.2400
34	0.0064	0.19	6.33	2.312	0.1967

TABLE A4.2 – TENSILE TESTING OF SISAL FIBRES

Samples	Weight [g]	Linear Mass [Tex]	Maximum Strength [N]	Maximum Elongation [%]	Tensile Stress [N/Tex]
35	0.0151	0.43	20.93	3.300	0.2757
36	0.0096	0.27	17.00	2.440	0.3551
37	0.0059	0.16	8.08	2.712	0.2737
39	0.0053	0.14	5.18	6.470	0.1948
40	0.0063	0.16	12.83	3.316	0.4071
41	0.0063	0.15	14.58	2.568	0.4627
42	0.0103	0.25	12.58	8.150	0.2428
43	0.0096	0.22	16.58	2.288	0.3462
44	0.0100	0.23	18.00	2.568	0.3600
45	0.0070	0.16	15.58	2.888	0.4450
46	0.0047	0.10	9.08	1.978	0.3872
47	0.0119	0.25	15.93	2.400	0.2681
48	0.0074	0.15	15.43	4.250	0.4179
49	0.0076	0.16	13.08	2.580	0.3432
50	0.0095	0.19	17.18	2.440	0.3607

Note: Sample 38 was invalid.

ATTACHMENT 5 – FLEXURAL STRENGTH TESTING RESULTS**TABLE A5.1 – RESULTS FROM FLEXURAL TESTING**

Sample		Maximum Load (N)		
		Sample 1	Sample 2	Sample 3
Plain Cement Mortar		3082.66	-	-
No Surfactant	0.2% MCC	2953.19	2819.81	2700.13
	0.5% MCC	3335.40	3432.27	3051.21
	0.75% MCC	2883.17	2870.80	2687.57
	0.25% Sisal	2716.47	2754.96	2715.85
	0.5% Sisal	2802.35	2856.89	3156.02
	0.25% Sisal + 0.2% MCC	2611.53	2327.46	2357.42
	0.25% Sisal + 0.5% MCC	2584.33	2526.95	2677.03
	0.25% Sisal + 0.75% MCC	2385.82	2598.54	2180.31
20% Pluronic F127	0.2% MCC	2809.26	-	2613.62
	0.5% MCC	4061.87	-	-
	0.75% MCC	2644.53	2629.30	2551.63
	0.25% Sisal	2790.24	2942.68	2739.97
	0.5% Sisal	2417.41	2799.36	2556.58
	0.25% Sisal + 0.2% MCC	2832.35	2659.96	2736.19
	0.25% Sisal + 0.5% MCC	2735.79	2497.16	2385.80
	0.25% Sisal + 0.75% MCC	2435.94	2224.33	2505.19
40% CTAB	0.2% MCC	1445.29	1675.54	1543.63
	0.5% MCC	1661.69	1637.87	1723.71
	0.75% MCC	1162.71	1436.60	1105.86
	0.25% Sisal	-	2116.95	1867.09
	0.5% Sisal	2103.74	2251.39	1994.67
	0.25% Sisal + 0.2% MCC	-	2392.58	2580.96
	0.25% Sisal + 0.5% MCC	1837.74	1656.41	1957.74
	0.25% Sisal + 0.75% MCC	-	1675.81	1607.93
100% CTAB	0.25% Sisal + 0.2% MCC	2078.33	-	2030.57
	0.25% Sisal + 0.5% MCC	2072.98	2349.74	2255.73

ATTACHMENT 6 – COMPRESSIVE STRENGTH TESTING RESULTS

TABLE A6.1 – RESULTS FROM COMPRESSIVE TESTING

Sample		Maximum Load (kN)					
		Sample 1		Sample 2		Sample 3	
Plain Mortar		56.33	42.65	60.93	56.87	54.00	46.25
No Surfactant	0.2% MCC	42.45	47.75	43.77	45.08	46.83	42.32
	0.5% MCC	57.32	57.35	55.91	57.07	53.36	55.51
	0.75% MCC	58.38	54.59	56.18	54.65	55.32	53.17
	0.25% Sisal	53.91	51.98	53.94	54.52	48.17	51.59
	0.5% Sisal	47.08	52.28	47.59	52.25	51.24	54.70
	0.25% Sisal + 0.2% MCC	40.53	46.19	48.14	43.88	46.52	43.83
	0.25% Sisal + 0.5% MCC	45.89	44.34	50.10	45.69	50.17	55.66
	0.25% Sisal + 0.75% MCC	42.04	48.36	47.71	50.41	56.25	43.21
20% Pluronic F127	0.2% MCC	43.92	40.46	47.64	41.84	49.61	45.66
	0.5% MCC	61.46	63.59	62.21	65.21	61.48	65.18
	0.75% MCC	45.31	50.20	47.86	51.06	48.03	52.28
	0.25% Sisal	49.41	50.92	51.97	54.34	48.88	45.76
	0.5% Sisal	48.08	52.78	45.16	49.92	51.90	53.01
	0.25% Sisal + 0.2% MCC	40.05	52.35	47.98	50.39	45.99	52.60
	0.25% Sisal + 0.5% MCC	58.04	43.59	58.80	62.72	56.91	56.63
	0.25% Sisal + 0.75% MCC	44.25	48.86	53.78	53.22	51.47	47.35
40% CTAB	0.2% MCC	20.89	19.80	17.34	18.95	21.25	20.09
	0.5% MCC	24.81	25.53	22.72	24.54	26.09	23.75
	0.75% MCC	11.29	15.23	15.32	12.77	13.40	12.56
	0.25% Sisal	20.53	-	21.51	20.21	23.30	25.51
	0.5% Sisal	23.43	26.48	27.57	26.58	25.44	28.71
	0.25% Sisal + 0.2% MCC	43.24	39.67	41.01	38.14	39.70	39.75
	0.25% Sisal + 0.5% MCC	19.42	20.20	21.21	20.17	20.94	19.48
	0.25% Sisal + 0.75% MCC	16.02	19.54	15.97	16.52	15.05	14.59
100% CTAB	0.25% Sisal + 0.2% MCC	20.93	27.00	28.46	24.67	29.03	27.97
	0.25% Sisal + 0.5% MCC	29.12	33.68	27.74	28.07	30.85	29.83

ATTACHMENT 7 – WEIGHT AND DENSITY

TABLE A7.1 – WEIGHT AND DENSITY VALUES

Sample		Weight (g)				Density (g/cm ³)
		Sample 1	Sample 2	Sample 3	Average	
Plain Mortar		568.0	578.0	569.0	571.7	2.23
No Surfactant	0.2% MCC	573.0	571.7	572.1	572.3	2.24
	0.5% MCC	566.3	565.4	566.9	566.2	2.21
	0.75% MCC	576.9	571.8	575.0	574.6	2.24
	0.25% Sisal	569.2	569.6	569.3	569.3	2.22
	0.5% Sisal	588.0	583.3	580.4	583.9	2.28
	0.25% Sisal + 0.2% MCC	564.9	563.5	564.9	564.4	2.20
	0.25% Sisal + 0.5% MCC	569.9	574.3	573.5	572.5	2.24
	0.25% Sisal + 0.75% MCC	571.0	582.6	571.1	574.9	2.25
20% Pluronic F127	0.2% MCC	570.0	569.0	576.4	571.8	2.23
	0.5% MCC	590.0	586.3	582.5	586.3	2.29
	0.75% MCC	571.1	570.5	572.8	571.5	2.23
	0.25% Sisal	582.8	574.7	584.6	580.7	2.27
	0.5% Sisal	582.4	580.5	582.5	581.8	2.27
	0.25% Sisal + 0.2% MCC	574.3	574.4	577.8	575.5	2.25
	0.25% Sisal + 0.5% MCC	582.1	581.8	575.7	579.9	2.27
	0.25% Sisal + 0.75% MCC	583.6	584.8	588.5	585.6	2.29
40% CTAB	0.2% MCC	491.8	485.6	486.5	487.9	1.91
	0.5% MCC	503.3	504.9	500.9	503.0	1.96
	0.75% MCC	466.3	487.5	469.6	474.5	1.85
	0.25% Sisal	496.1	516.1	494.8	502.3	1.96
	0.5% Sisal	510.8	506.6	508.9	508.8	1.99
	0.25% Sisal + 0.2% MCC	559.5	560.5	563.9	561.3	2.19
	0.25% Sisal + 0.5% MCC	508.3	492.3	503.1	501.2	1.96
	0.25% Sisal + 0.75% MCC	511.9	495.1	489.1	498.7	1.95
100% CTAB	0.25% Sisal + 0.2% MCC	523.0	513.3	506.9	514.4	2.01
	0.25% Sisal + 0.5% MCC	516.0	516.3	513.9	515.4	2.01