

THERMORESPONSIVE, SHORT ELECTROSPUN FIBRE SPONGES FOR APPLICATION IN ROOF TOP AIR-WATER HARVESTING

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND

The thermoresponsive nature of Poly(N-isopropylacrylamide) (PNIPAm) and its composites has been well reported in literature. Even though very little has been done of the harnessing of this trait in the capture of atmospheric water reserves, a lot has been reported in the biomedical field. According to newly published research by Massachusetts Institute of Technology, University of California-Berkeley, Saudi Arabia, atmospheric water is a resource equivalent to ~10% of all fresh water in lakes on Earth. However, an efficient process for capturing and delivering water from air, especially at low humidity levels (down to 20%), has not been developed. The water absorption capacity of thermo-responsive sponges can be considerably altered by small changes in temperature because their polymer chains change from hydrophilic to hydrophobic above their low critical solution temperature (LCST). This process is illustrated in **Figure 1**. The main aim of this study is to synthesize ultralight, sponge-like cellulose-based mat which can absorb atmospheric water from a humid atmosphere at low temperatures and release it when the temperature is increased (typical night/day temperature variations).

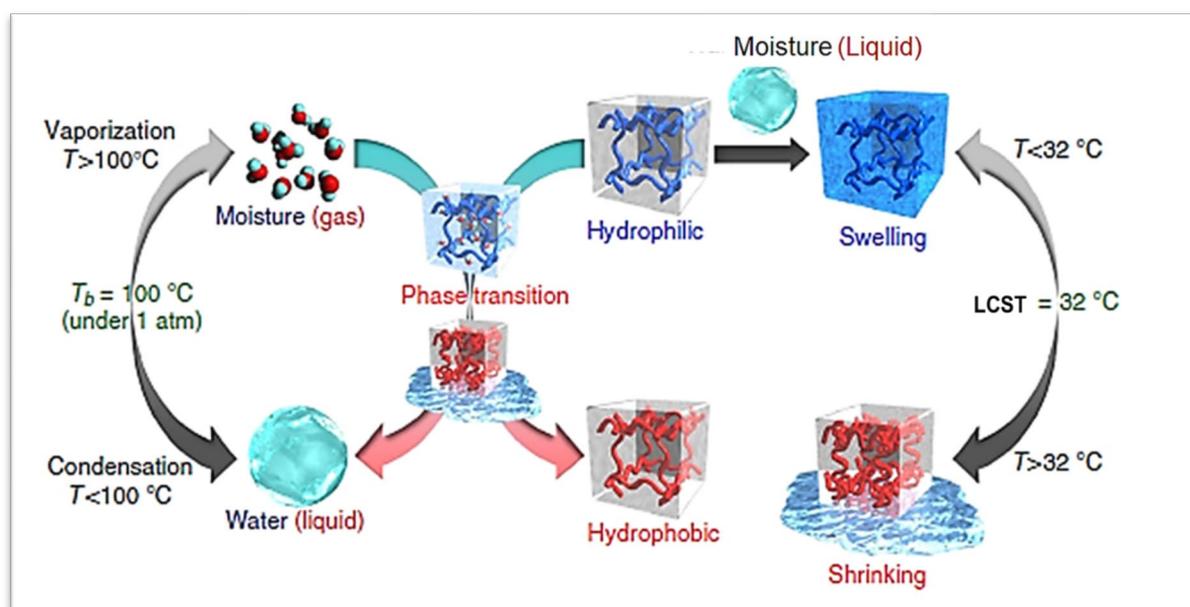


Figure 1: Conceptual illustration of this study: air water absorption and release behaviour of cellulose-PNIPAm sponges (Figure adapted from Matsumoto, 2018).

AIMS AND OBJECTIVES OF THIS STUDY

Research on the fabrication of composites of PNIPAm with synthetic and natural polymers is widespread. From an environmental point of view, natural polymers are advantageous compared to their synthetic counterparts. This study was aimed at the fabrication of thermoresponsive sponges for application in rooftop air-water harvesting. The objectives of this study were as follows.

1. To produce cellulose nanofibres using the electrospinning technique. Cellulose will be obtained from sugarcane bagasse which is a by-product (waste) of the sugar manufacturing industry in South Africa. Environmentally friendly solvents will be prioritized in the whole process.
2. To graft poly(-N-isopropylacrylamide) (PNIPAm) onto cellulose nanofibres for thermoresponsive behaviour. The cellulose nanofibres will be responsible for mechanical stability. Several polymer block ratios will be investigated to attain maximum water absorption and temperature sensitivity.
3. To fully characterise the fabricated nanofibres using several spectroscopic techniques including Fourier transform infra-red spectroscopy (FTIR), and thermogravimetric analysis (TGA).
4. To produce short electrospun fibre sponges from the prepared nanofibres.
5. To study the morphology of all the materials using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
6. To conduct air-water absorption studies. The fibres are expected to absorb atmospheric water at low temperatures and release the water above the lower critical solution temperature (LCST) of the thermoresponsive polymers.

METHODS

Extraction of Cellulose nanofibres (CNFs)

Cellulose was successfully obtained via two routes (deacetylation of cellulose acetate and extraction from sugarcane bagasse). Successful extraction was confirmed using Fourier Transform Infra-Red Spectroscopy (FTIR).

Fabrication of PNIPAm/CNFs composites

PNIPAm synthesis using Free Radical polymerization: A typical Free radical polymerization procedure for synthesizing PNIPAm was performed by dispersing NIPAM in ethanol under the protection of N₂ flow. The initiator Azobisisobutyronitrile (AIBN) was then added and the polymerization was carried out at 60°C for 6 h. The polymer was precipitated in a large excess of ether, and the white polymer was collected by filtration and dried at 40°C under vacuum overnight. The weight of the polymer as confirmed by size exclusion chromatography (SEC) was 40000.

Sponge fabrication: The cellulose was then modified with PNIPAm to induce thermoresponsive properties. A series of CNFs/PNIPAm composite aerogels were fabricated via the preparation of PNIPAm modified CNF suspensions with varying ratios concentrations PNIPAm. Unmodified CNF aerogels were also prepared as a negative control as well as a positive control with only PNIPAm. Each sample was thoroughly mixed using magnetic stirring. This was followed by rapid freezing in liquid nitrogen (-196°C) and freeze-drying. The

freeze-drying process was maintained at -50°C for 72 h to obtain lightweight sponge-like aerogels with well-defined shape.

ATMOSPHERIC WATER HARVESTING EXPERIMENTS AND RESULTS

Laboratory controlled experiments indicated lab-scale have demonstrated exceptionally positive results with the sponges absorbing up to 15X their weight while outdoor experiments demonstrated an average of 8 times the sponge weight with maximum absorptions of up to 12 times on very humid conditions.

ACKNOWLEDGEMENTS

The project team wishes to thank the following people for their contributions to the project:

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- Mr Mohamed Jaffer (Chemical Engineering Department at the University of Cape Town) for Microscopy Imaging (SEM, TEM) assistance.

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Publications

1. NP Gule, Natural polymers in water treatment – A review: Submitted to Polymers – Under review.

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1. NP Gule: Advances in Water Research panel session. South Africa-Sweden University Forum (SASUF) 23-27 November, SASUF Goes Digital: 2020 Edition.

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ACRONYMS & ABBREVIATIONS

AIBN	Azobisisobutyronitrile
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infra-Red
CA	Cellulose acetate
CNFs	Cellulose nanofibres
DMAc	Dimethylacetamide
DMF	dimethylformamide
DSC	Differential Scanning Calorimetry
EDX	energy-dispersive X-ray
ES	Electrospinning
FWCS	Fog Water Collection System
HCl	Hydrochloric acid
LCST	Lower Critical Solution Temperature
NF	nanofiltration
PNIPAm	Poly(N-isopropylacrylamide)
ROP	ring-opening polymerisation
SEM	scanning electron microscope
TEM	transmission electron microscopy
TGA	Thermogravimetric analysis
UCST	Upper critical solution temperature
<i>W</i>	wet weight

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

Thermo-responsive hydrogels and aerogels such as poly(N-isopropylacrylamide) (PNIPAm) based ones have attracted considerable interest in recent years [1-3]. Their response to slight changes in temperature which makes them applicable in a variety of fields. PNIPAm gels, which have a lower critical solution temperature (LCST) of around 32°C, drastically change their hydrophilicity/hydrophobicity at their LCST [2]. PNIPAm hydrogels have been extensively studied for sensing, drug delivery, and cell cultures. The drastic changes in the hydrophilicity/hydrophobicity and volume of PNIPAm hydrogels are observed in aqueous solutions. Although such thermoresponsiveness and various applications of PNIPAm hydrogels in aqueous media are well known, many researchers have never observed unique thermo-responsive behaviour of the dried PNIPAm gels in air. Very few studies have been conducted on the of the applications of PNIPAm and its composites in their dried states [4-8] This study reports that dried sponge-like materials containing PNIPAm can be applied as thermo-responsive moisture absorbents under relatively humid conditions.

1.2 PROJECT AIMS

The main aim of this study is to synthesize ultralight, sponge-like cellulose-based mat which can absorb atmospheric water from a humid atmosphere at low temperatures and release it when the temperature is increased (typical night/day temperature variations). The objectives of this study are as follows.

1. To produce cellulose nanofibres using the electrospinning technique. Cellulose will be obtained from sugarcane bagasse which is a by-product (waste) of the sugar manufacturing industry in South Africa. Environmentally friendly solvents will be prioritized in the whole process.
2. To graft poly(-N-isopropylacrylamide) (PNIPAm) onto cellulose nanofibres for thermoresponsive behaviour. The cellulose nanofibres will be responsible for mechanical stability. Several polymer block ratios will be investigated to attain maximum water absorption and temperature sensitivity.
3. To fully characterize the fabricated nanofibres using several spectroscopic techniques including Fourier transform infra-red spectroscopy (FTIR), and thermogravimetric analysis (TGA).
4. To produce short electrospun fibre sponges from the prepared nanofibres.
5. To study the morphology of all the materials using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
6. To conduct air-water absorption studies. The fibres are expected to absorb atmospheric water at low temperatures and release the water above the lower critical solution temperature (LCST) of the thermoresponsive polymers.

1.3 REPORT LAYOUT

The report is presented as follows:

Chapter 1: Chapter 1 introduces the study by means of a background to the problem statement and the motivation for the study. The aim and scope of the study, as well as the structure of the report are also presented in this chapter.

Chapter 2: In this chapter, the global water crisis is explained and contributing agents as well as ways to mitigate the issues propagating the problem. This is followed by an in-depth discussion on the several ways

which have been investigated to augment available water globally. This brings us to the subject of air water harvesting. This subject is discussed in detail.

Chapter 3: in this chapter, the extraction of cellulose, preparation and characterization of thermoresponsive sponges is reported.

Chapter 4: In Chapter 4, the application envisaged for these sponges is tested. The atmospheric water harvesting capacity of the sponges is evaluated. This was done in the lab and in an outdoor environment.

Chapter 5: Highlights the achievements of the project as well as future work recommendations.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, the global water crisis is explained and contributing agents as well as ways to mitigate the issues propagating the problem. This is followed by an in-depth discussion on the several ways which have been investigated to augment available water globally. This brings us to the subject of air water harvesting. Several researchers have identified this resource as an important key to clean water access. A review of literature on air-water harvesting is presented. The second part of this section focusses on the technical aspects of this study. Thermoresponsive nanomaterials are discussed with specific focus on natural polymers. The natural polymer, cellulose is discussed. Advantages of using natural polymers over their synthetic counterparts are also highlighted. This section further expands on advances in electrospinning and venturing into short electrospun nanofibres which is the technique that will be used to fabricate the polymer sponges in this project. Figure 2-1 illustrates the structure of this chapter.

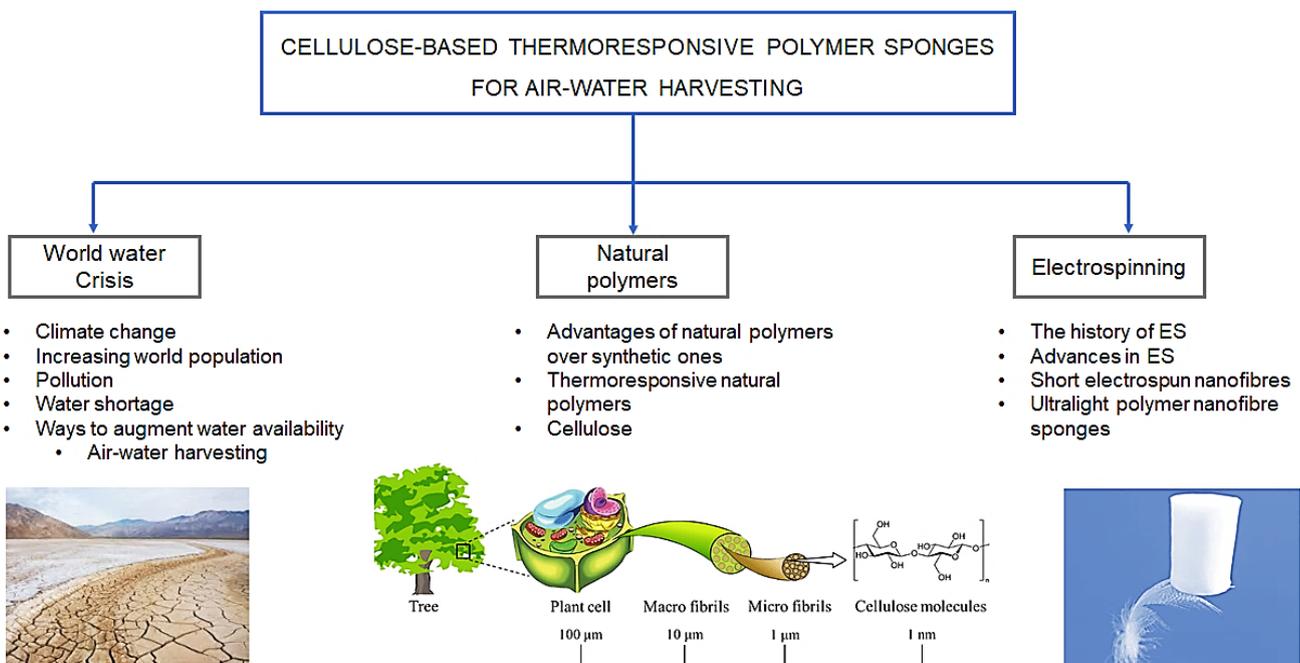


Figure 2-1: Overview of topics discussed in the literature review.

2.2 THE GLOBAL WATER CRISIS/ WATER AVAILABILITY

Lack of access to safe drinking water is one of the major concerns facing humanity. A large percentage of all water in our planet is salt (about 97%) and less than 3% is freshwater. Of the 3% fresh water, about 80% is frozen in glaciers, ice caps, or is deep underground in aquifers. Less than 1% of Earth's water is freshwater that is easily accessible to us to meet our needs, and most of that water is replenished by precipitation (a vital component of the water cycle, affecting every living thing on Earth). Water vapour as shown in Figure 2-2 contains more water than all the rivers of the earth combined. According to the United Nations, more than 1.2 billion people lack access to adequate quantities of water and another 500 million people are approaching this

situation. (Human Development Report 2006. UNDP, 2006) [9] Water scarcity is one of the most important threats facing humanity. The increasing global population, urbanization and industrialization will further increase water demands in the future. Furthermore, climate change and anticipated increases in extreme weather events will result in an intensification in drought (frequency, severity and duration) which will further deplete water resources [9].

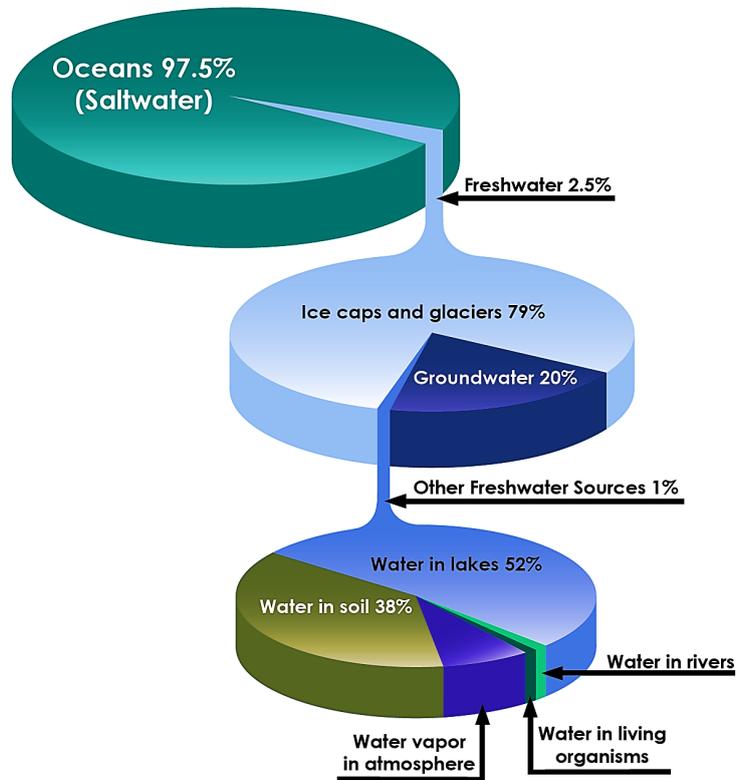


Figure 2-2: Break down of the earth's water supply.

2.3 CLIMATE CHANGE

Over the last decade, several studies shown an increase in the prevalence and severity of drought and other extreme weather conditions. The phenomenon of climate change will increasingly alter natural cycles at a global level and affect natural ecosystems and human development in harmful ways. Its effects are manifested in the disruption of the hydrological cycle combined with increasing temperature and precipitations' fluctuations. Numerous studies have proven that climate change is caused by greenhouse gas (GHG) emissions mainly originating in industrialized countries. The impact of climate change extends to both developed and developing countries. The impact of climate change affects all sectors and levels of the global society. The impact, however, can be felt more intensely for the developing countries of the world and South Africa, as a developing country, does not have the means to cope with the hazards associated with climate change [9] Climate change has brought about extreme weather events like droughts and floods which are impacting both water quality and availability through changes in rainfall patterns. With more-intense storms, floods and droughts; changes in soil moisture and runoff; and the effects of increasing evaporation and changing temperatures on aquatic systems comes major challenges threatening the human race. Figure 2.3 illustrates some of the harsh environmental impacts associated with climate change.

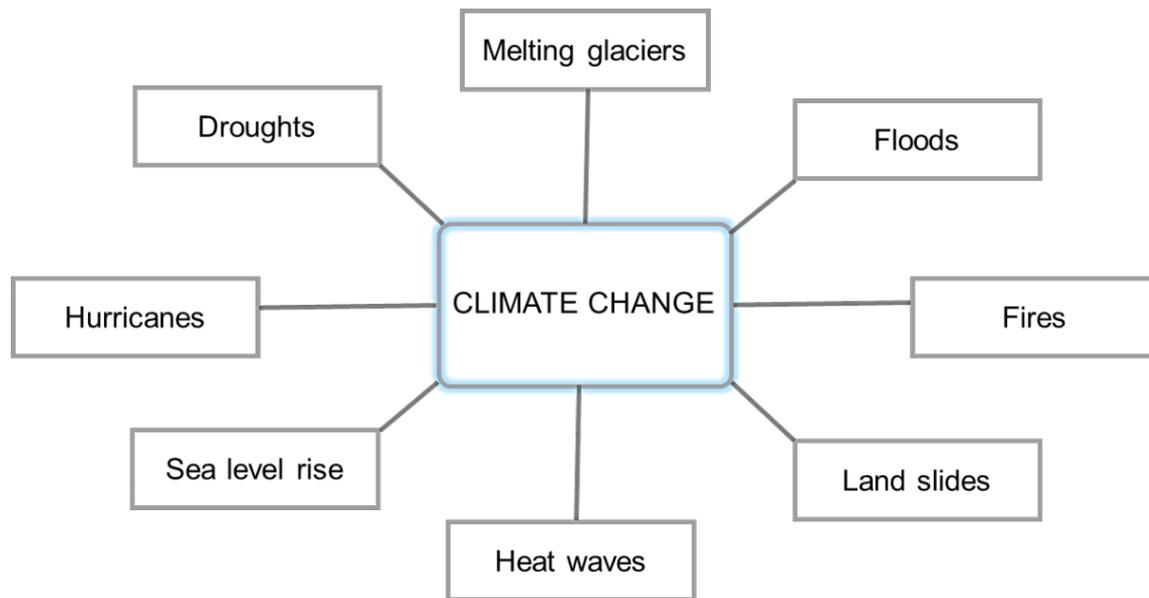
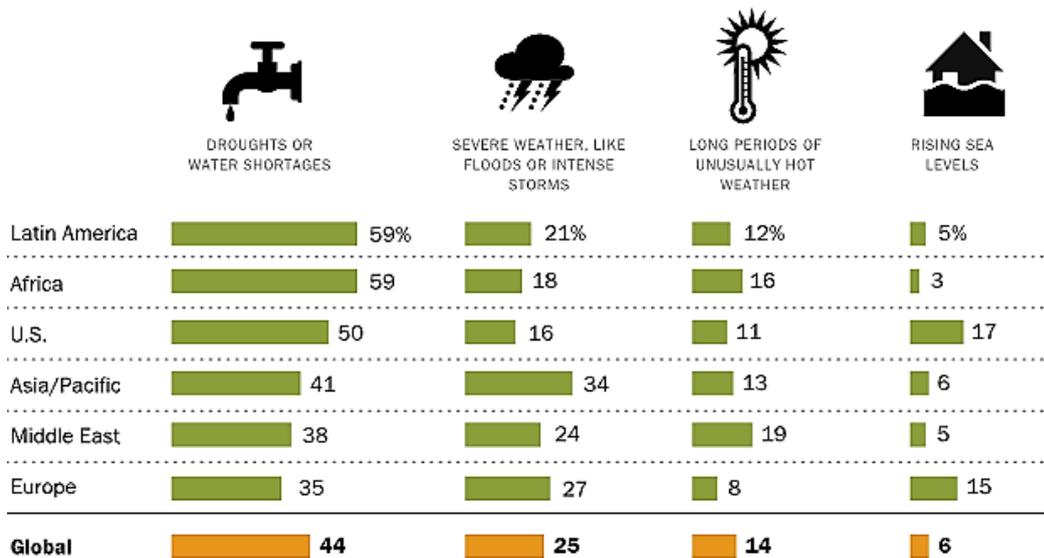


Figure 2-3: Effects of climate change

From the data presented in Figure 2-4, it is evident that Africa is one of the continents severely affected by climate change and that access to water is by far one of the major effects facing the continent. According to the National Water Resource Strategy, the variability in water availability is by far the severest medium through which the impacts of climate change are being experienced in South Africa. This decrease in water availability is associated with crop losses which impacts food security, water restrictions hampering directly on the basic human right of access to clean water. The water cycle is expected to be altered in important ways by this phenomenon. The uneven distribution of this resource throughout the year will affect societies in numerous ways, as water is a central resource that supports human activities and ecosystems. The agriculture sector, among others, is extremely vulnerable to climate change due to the constraints it can have on the hydrological cycle and the availability of water. The likelihood that already existing water related problems will worsen are high, therefore the clear next step is to adapt to future conditions. Finding ways to supplement available water resources has become very important.

Drought Tops Climate Change Concerns across All Regions

Regional medians of most concerning effects of global climate change



Note: Russia and Ukraine not included in Europe median.

Source: Spring 2015 Global Attitudes survey, Q43.

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Figure 2-4: Statistical data on the effects of climate change.

2.4 AIR WATER HARVESTING

According to Figure 2-2 there is more water in the atmosphere than water in the dams and rivers combined. Over the past 4 centuries, the interest in atmospheric or air water has seen drastic increase. Atmospheric “air” water was first acknowledged more than 400 years ago, in the Canary Islands, the existence of a tree that supplied the inhabitants with sufficient water was reported by Duret in 1605 (Figure 2-5), and by Bauhin and Cherler in 1610. Duret also reported that there was no other water source in the islands. This wonder tree was called ‘Rain tree’ (mentioned in Hutchinson, 1919). It was later established that the rain trees or fountain trees collected fog or mist water with their leaves [10].



Figure 2-5: Rain tree of the Canary Islands as shown by Duret in *Histoire Admirable* in 1605 (Photo: Wilhelm Barthlott). [10]

Over time, the harvesting of atmospheric water also referred to as ‘fog collection’ came into the limelight (Figure 2-6). Several fog-collection methods were investigated and these included the interception and utilization of intercepted fog by trees and the construction of mound-like different structures in dry regions. Cisterns were also reportedly built under trees in mountain areas in Oman to collect fog. In the desert areas of Mediterranean and South America, e.g. in the Atacama Desert, different artificial structures, for example stone piles were used to collect mist and dew. However, the scientific study of fog collection began at the beginning of the 20th century in the Table Mountains of South Africa. Marloth, one of the pioneers of fog-collection research, used plants, resembling reeds, above one of the two rain gauges to measure fog precipitation [10]. Although fog forms the major source of water for plants and animals in arid areas such as the Namib and the Atacama deserts, it was until recently an unexploited source of water for domestic purposes. Since the 1980s, fog harvesting has been explored in many other parts of the world and a lot of research has been conducted in this area. Successful fog harvesting projects have been established in arid countries such as Chile, Venezuela, Guatemala, Peru, Ecuador, Eritrea, Iran, Spain, the Sultanate of Oman, Colombia, Nepal and Morocco. Several other ways of harvesting atmospheric water have been explored [10]



Figure 2-6: Left: Fog Water Collection System (FWCS) at Mariepskop (1969) (Schutte, 1971). Right: Test fog water collectors at Cape Columbine lighthouse during the research that was conducted in 1995. The ‘standard’ 1 m² fog water collector is shown to the left. The larger test system on the right was donated by a private individual (Maarten van Schoor) and was only deployed at Cape Columbine [10].

2.4.1 Advances in air-water harvesting.

According to newly published research by Massachusetts Institute of Technology, University of California-Berkeley, Saudi Arabia, atmospheric water is a resource equivalent to ~10% of all fresh water in lakes on Earth. However, an efficient process for capturing and delivering water from air, especially at low humidity levels (down to 20%), has not been developed [11]. Statistics indicate that by the year 2040, water, which is already a scarce resource globally, will be even scarcer. In 2016-2018, Cape Town for example, faced one of its worst droughts in more than 100 years. This lack of precipitation calls for innovative ways to harvest or obtain water from alternative resources and atmospheric air is one of the almost untouched resources from which water can be harvested. As indicated in Figure 2-2, atmospheric water accounts for more fresh water than all rivers and dams combined.

2.4.2 Advances in Electrospinning and the dawn of 3D nanostructured materials

ES is an efficient technique to make fibres with diameters fluctuating from a few nanometers to a few micrometers. The ES process is relatively simple, suitable, constructive and extensively applied for the production of nanofibrous membranes. The development of fibres through ES depends on uniaxial stretching

of a viscoelastic jet manufactured from a polymer solution. Figure 2-7 is a schematic diagram of the basic system used for single needle ES. Three major substances are examined in the ES setup: a high voltage power supply; a spinneret, which is a needle; and then the collector (aluminium foil).

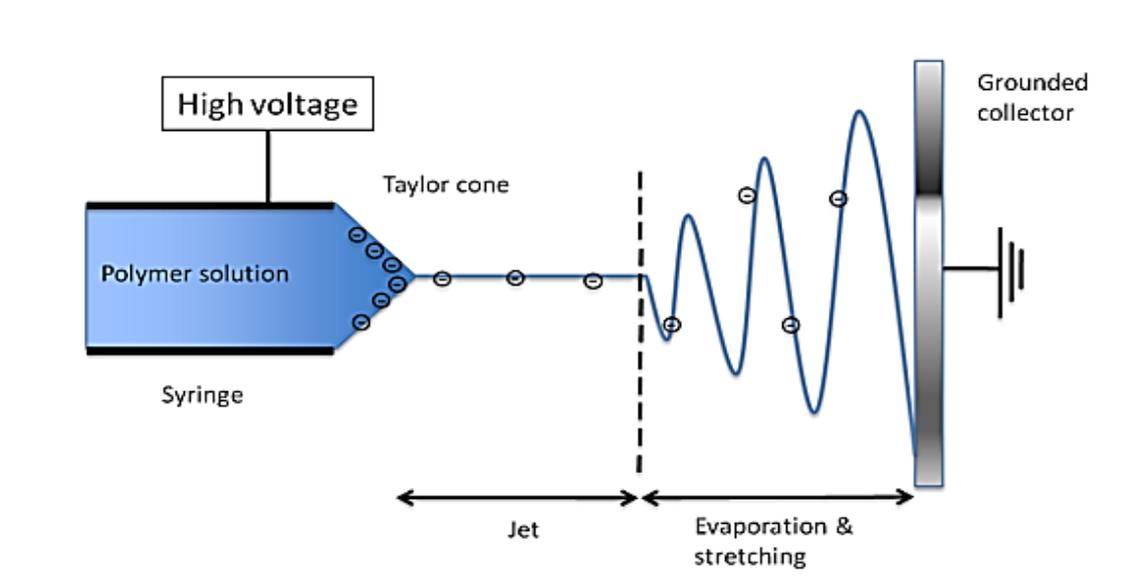


Figure 2-7: Schematic diagram of ES setup [12].

Advances in ES have allowed for a migration from the flat morphologies fabricated through the conventional layer by layer manufacturing process. An indirect approach for making 3D porous materials with a porosity of more than 99% is through the utilization of a dispersion of short electrospun fibres and freeze-drying. Electrospinning produces long and continuous fibres and these can be cut by mechanical means followed by dispersing them in appropriate solvents and subsequent lyophilization to obtain 3D sponges. This process is demonstrated in Figure 2-8 and the resulting materials are generally reversibly compressible, flexible and ultra-light as indicated by the example in Figure 2-9. This process is easily scalable.

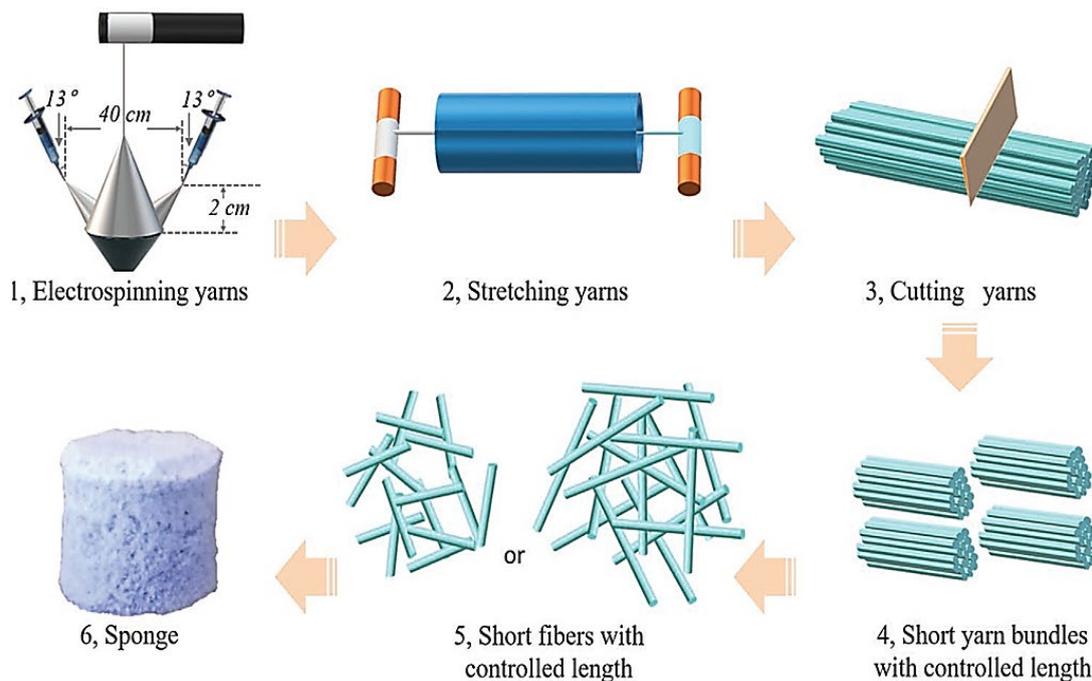


Figure 2-8: Fabrication of 3D sponges through the dispersion of short electrospun nanofibres [7].

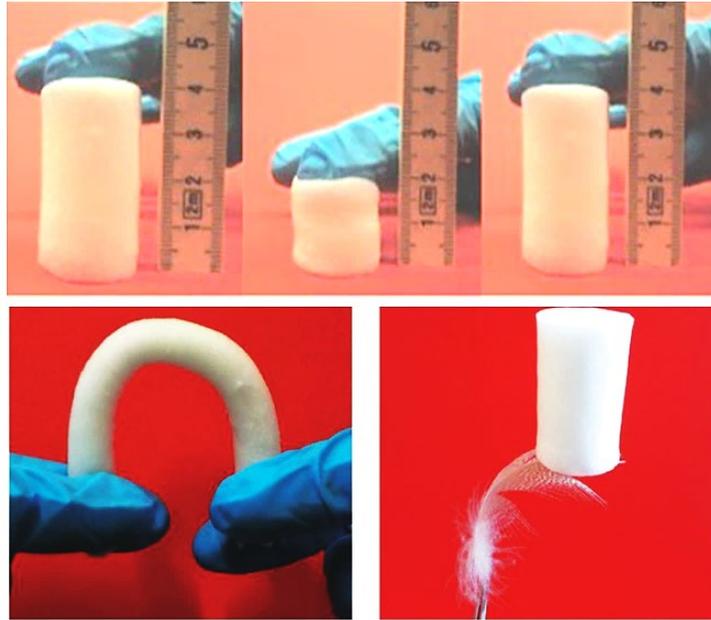


Figure 2-9: Ultralight compressible and flexible 3D structured materials [7].

In the short fibre dispersion stage, the process for attaining these 3D structures takes place in 3 stages which are the solvent exchange stage, the freezing stage (flash drying in liquid nitrogen) and the drying stage (freeze drying) and these are demonstrated in Figure 2-10.

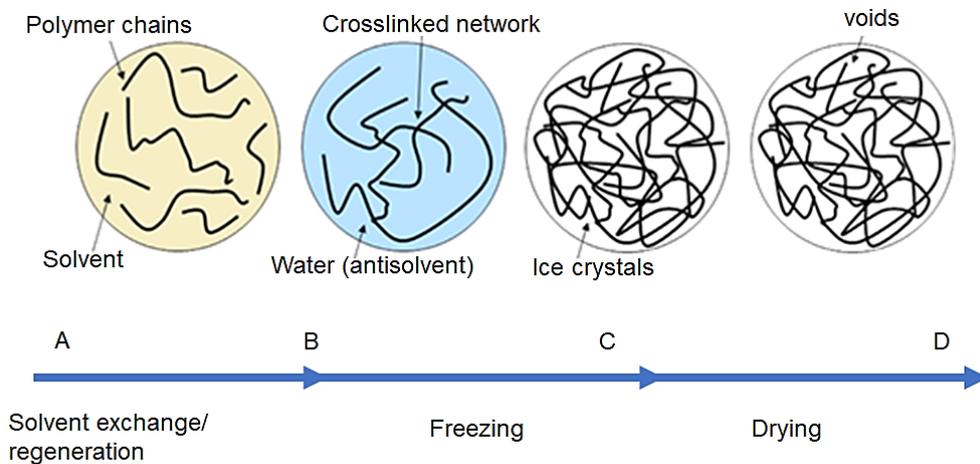


Figure 2-10: Processing of polymer sponges from short electrospun fibres (a,b) mechanism of solvent exchange, (b,c) freezing and finally (c,d) drying

2.5 THERMORESPONSIVE POLYMERS

The field of smart materials has exponentially gained interest in recent years. “Smart” materials are generally based on the existence of a stimuli-responsive polymer. Stimuli-responsive polymers are polymers with properties designed to sharply and quickly respond to small physical or chemical environmental changes.

These responses are dictated by the functional groups present within or on polymer chain. At the macromolecular level, polymer chains can be modified in different ways such as, hydrophilic-to-hydrophobic balance, conformation, solubility, degradation, and bond cleaving. Over the few decades, these polymers have found applications in several fields of material science including drug delivery, tissue engineering, bio-sensing diagnostics, smart coatings and others [13-19]. Figure 2-11 presents some common stimuli-responsive polymers and a selection of polymers and functional groups which exhibit stimuli-responsive behaviour and these are discussed in the following sections.

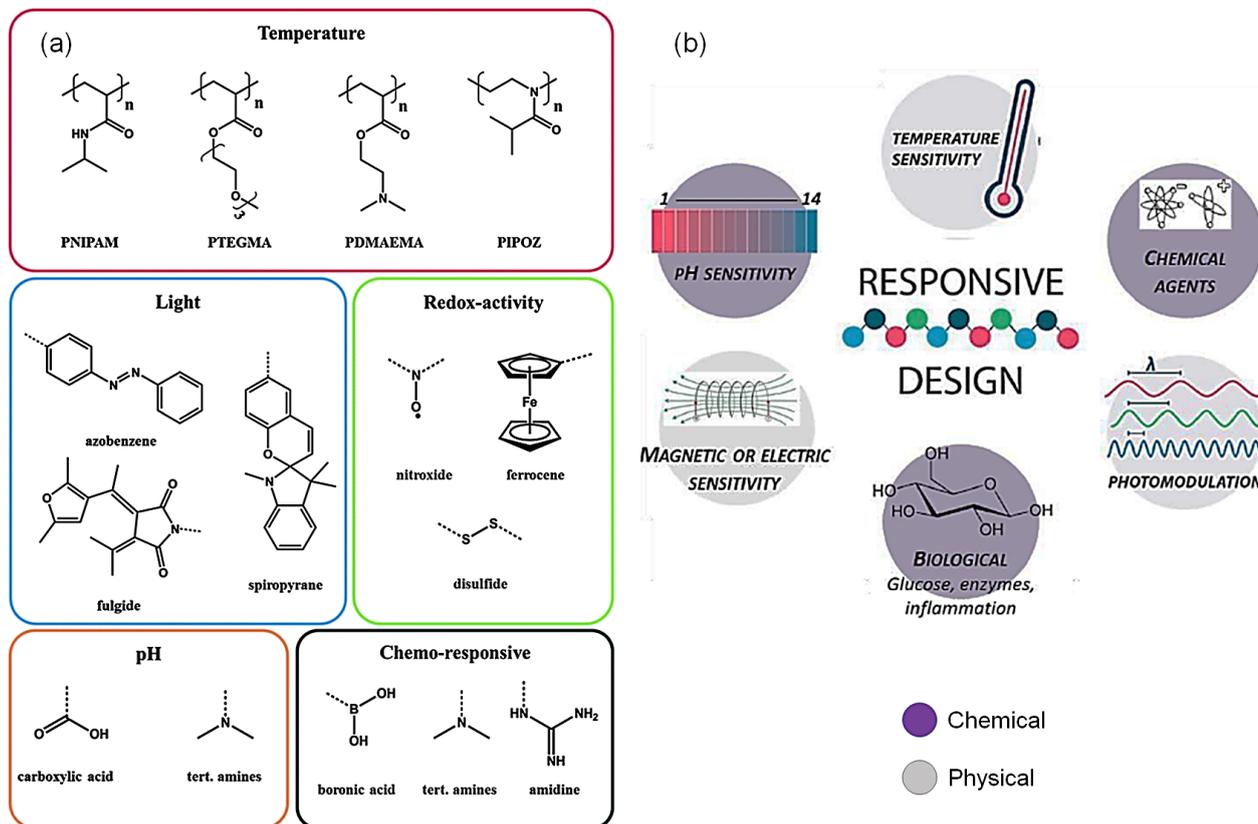


Figure 2-11: (a) Selection of important polymers and functional groups, exhibiting stimuli-responsive behaviour [14] (b) Classification of stimuli for stimuli-responsive polymers (adapted from [17]).

2.5.1 Photo - UV-light responsive polymers

These polymers are sensitive to light exposure at a specific wavelength. Common examples of photo-responsive polymer contain light-sensitive chromophores such as azobenzene groups, spiropyran groups or nitrobenzyl groups [20-22].

2.5.2 pH responsive polymers

These polymers have the ability to donate or accept protons during changes in pH conditions. Changes in pH trigger ionic interactions on the polymer which can result in either an extension or collapsing of the polymer

chain in aqueous media. Typical pH responsive polymers which exhibit very quick/rapid protonation-deprotonation functionalities are carboxylic and amino groups [23-24].

2.5.3 Redox responsive polymers

This group of polymers contain a functional electrochemical address “stimulus” of the redox-sensitive group, which causes a change in its oxidation state. Some of these polymers can react to electric impulses and oxidize or reduce inducing a hydrophilic/phobic inversion like with ferrocene or disulfides. For example, polymers with disulfide groups are degraded when exposed to cysteine or glutathione, which are reductive amino-acid based molecules [25-27].

2.5.4 Chemical responsive polymers

These stimuli-responsive polymers are sensitive to chemical changes in the environment. Boronic acid is an example. It is sensitive to diols and has a particular application in a reaction with glucose. The diol sensitivity is based on the existence of a neutral form and an anionic form of boronic acid. In the neutral form boronic acid is hydrophobic. The anionic species can link diols in a reversible reaction inducing an increase of the polymer hydrophilicity. Alginate can be another example which uses the presence of cations to completely modify its behaviour by crosslinking [28-29].

2.5.5 Temperature responsive polymers

Temperature responsive polymers also known as thermo-responsive polymers are sensitive to a change in external temperature. This group of stimuli responsive polymers has gained a lot of interest because temperature changes can easily be applied to a system externally. Several applications of these polymers have been reported and these include applications in tissue engineering, drug delivery, catalysis, surface engineering among others [14,17,30-31].

The main characteristic features embodied by these polymers are a lower or upper critical solution temperature (LCST or UCST) around which the hydrophilic and hydrophobic interactions between the polymer and the aqueous media drastically change with very small changes in temperature. This phenomenon is driven by entropy to minimize the system's free energy.

2.6 THERMORESPONSIVE 3D POLYMERS / SPONGES

Recently ultralight porous 3D materials have attracted a lot of attention because of their 3D connected networks, high porosity, high flexibility and elasticity, and abundant material resources. These materials have been widely applied as electrode materials in the energy and sensor area, absorber materials including absorbing both gases and liquids, insulating materials (thermal, sound and electromagnetism), tissue engineering, oil/water separation, and many more [32-35]. In the published reports, three words, “sponge”, “aerogel” and “foam” are usually used to describe these ultralight porous 3D materials [7]. Depending on the material sources, ultralight porous 3D materials can be divided into four main classifications, including carbon-based, polymer-based, inorganic, and hybrid ultralight porous materials.

The group of Professor Agarwal at Bayreuth University has published a number of journal articles on functional and thermoresponsive electrospun nanofibrous materials. These materials include low density open cellular sponges with dual pore structure and densities of less than 100 mg cm⁻³ which pose both a challenge and an opportunity for advanced chemistry and material science. The challenge lies in the precise preparation of the sponges with property combinations that lead to novel applications [34]. The combination of the pore structure

and the material properties has led to exceptionally high water absorption capacity at low temperature and water release at elevated temperature. The porous structure of these materials provides fast mass transport for water absorption and desorption.

Short fibres can also be easily incorporated into the polymer matrix and flexible design methods can be applied to prepare short fibre reinforced composites. For any practical application in areas like water harvesting, there is a need for further research with respect to the ability of these materials to absorb water from humid air, making the absorption and release kinetics of water tuneable materials so that the same system can be used for water collection from atmosphere. Such a technology can also be applied as water reservoir for slow release for agricultural applications. Even though this field has not been extensively explored and few materials have been studied, the shortage of water in water stressed and economically underdeveloped areas requires simple and inexpensive alternatives. Research on cotton-like sponges and cellulose aerogels has been published and forms a basis for further research on the use using natural polymers to fabricate materials for water harvesting. Cellulose is the most abundant renewable biopolymer on the earth and makes up the bulk of plant cell walls since it is made by all plants. The hydroxyl groups in cellulose facilitate inter-molecular hydrogen bonding with other polymers, leading to novel functions and properties [4, 32].

The thermoresponsive ability of poly(N-isopropylacrylamide), PNIPAm on the other hand is well reported [36]. PNIPAm undergoes a coil-to-globule transition (hydrophilic-to-hydrophobic, respectively) in aqueous solution at a specific temperature (+32°C). The “grafting-from” approach to modify the surface of a cellulose mat using the thermoresponsive poly(N-isopropylacrylamide), PNIPAm, brushes will be explored in this study. The cellulose fibres will provide mechanical strength to the sponge while PNIPAm will contribute the temperature responsive properties.

2.7 NATURAL POLYMERS

Natural polymers are polymers derived from natural sources and hence biodegradable. They are biocompatible and non-toxic. Natural polymer composites are emerging very rapidly as the potential substitute to the metal or ceramic based materials in applications that also include the automotive, marine, sporting goods, and electronic industries [37]. The development of natural fibre composite materials or environmentally friendly composites has been a great topic recently due to the increasing environmental awareness [37-40]. Natural fibres are of interest to scientists due to advantageous traits such as low cost, high strength to weight ratio, low density per unit volume, non-corrosive property, and acceptable specific strength. In addition to their renewable and degradable characteristics [38]. They are often available at low cost as compared to synthetic fibres, and they cause less health and environmental problems for people producing the composites as compared to glass fibre-based composites. Natural fibres have been used in the development of highly thermally stable and acoustic insulator materials, they are also emerging as a feasible alternative to glass fibre composites in many applications such as automotive, boats, leisure, and constructions [38-41]. Natural polymers can be modified into different forms based on their functional groups [22-24]. Natural polymers will be prioritized in this study. The natural polymer of choice is cellulose which is the most abundant polymer on earth. Cellulose nanofibrous materials will be fabricated from sugarcane bagasse which is a waste product in the sugarcane manufacturing industry. The raw biomass is processed through a series of steps (dewaxing, alkali treatment, acid hydrolysis) to attain cellulose nanofibres as illustrated in Figure 2-12.

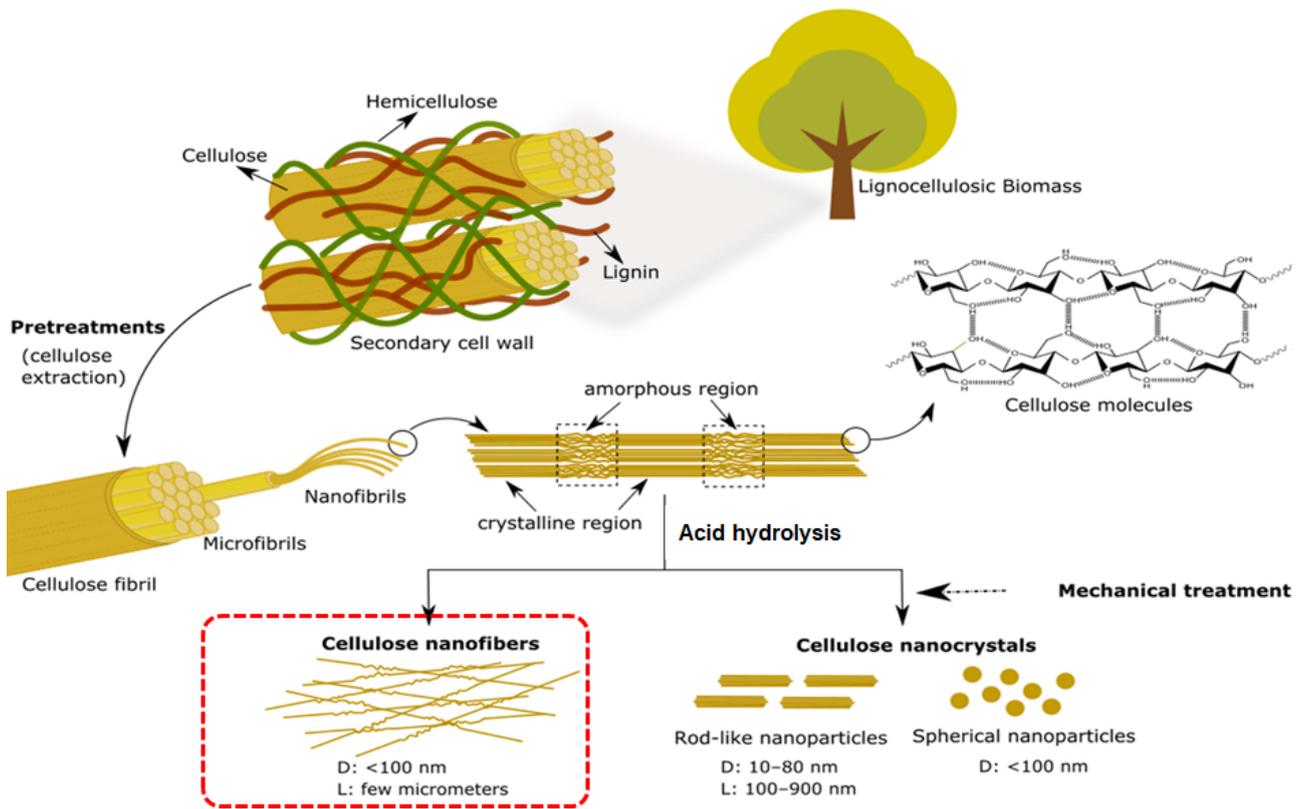


Figure 2-12: Process for CNFs production

CHAPTER 3: EXTRACTION OF CELLULOSE, PREPARATION AND CHARACTERIZATION OF THERMORESPONSIVE SPONGES

3.1 INTRODUCTION

Despite being the world's most abundant natural polymer and one of the most studied, cellulose is still a very challenging polymer. Cellulose is known to be insoluble in water and in many organic solvents, due to its high molecular weight and crystalline structure. This limits its electro-spinnability in most environmentally friendly solvents. In this section, we explore two techniques towards the fabrication of cellulose nanofibres.

- Extraction of cellulose from sugarcane bagasse
- Deacetylation of cellulose acetate to cellulose.

In this chapter, the methods used to obtain cellulose from the two sources are outlined. This is followed by a description of all the methods used towards the fabrication of the thermoresponsive sponges as well as the characterization techniques.

3.2 MATERIALS

Cellulose acetate (CA) was purchased from Merck, South Africa. N,N-dimethylacetamide (DMAc), acetone and NaOH were purchased from Sigma Aldrich, South Africa and used as received. N-isopropylacrylamine (NIPAm) was also purchased from Sigma Aldrich and purified by recrystallization. Sugarcane bagasse obtained from the KwaZulu-Natal province of South Africa was used as the starting material for CNFs extraction. N-Isopropylacrylamide (NIPAm), Sodium bromide (NaBr), 2, 2'-Azobis(isobutyronitrile) (AIBN), sodium hypochlorite (NaClO), hydrochloric acid (HCl), sodium hydroxide (NaOH), normal hexane, tertiary butanol, and ethyl alcohol were all purchased from Sigma Aldrich Ltd. Prior to use, NIPAm and AIBN were recrystallized three times in hexane and ethyl alcohol, respectively. No further purification was done for other reagents. All the reagents for PNIPAm synthesis were of analytical grade.

3.3 EXPERIMENTAL METHODS

3.3.1 Production of cellulose nanofibres using the electrospinning technique.

Two routes were evaluated:

- Deacetylation of cellulose acetate to cellulose.
- From bagasse which is a by-product (waste) of the sugar manufacturing industry in South Africa.

3.3.1.1 Cellulose from the deacetylation of cellulose acetate

Cellulose acetate (CA) is a natural polymer that is the most abundance derivative if cellulose and has been used in various applications including water treatment. The deacetylation of cellulose acetate yields cellulose. Cellulose acetate is electrospinnable in environmentally friendly solvents which makes the reverse engineering type process lucrative compared to the electrospinning of cellulose using harsh solvents like formic acid. To do this:

- Electrospinning of cellulose acetate

CA was electrospun in a binary solvent system (acetic acid/water (75/25)). The electrospinning conditions were adopted from previous literature. A syringe pump connected to the syringe. The electrospinning set-up consisted of variation of different distance, needle sizes (0.45 mm <ID< 0.90 mm) and high voltage supply (10-15 kV); and an aluminum collecting plate. Various concentrations of cellulose acetate (13%, 15% and 20%) were prepared and surface morphology of the electrospun nanofibre mats were investigated by SEM analysis.

- Deacetylation of CA:

A set of smooth nanofibre mats were utilized to generate cellulose nanofibre mats via alkaline deacetylation. The alkaline deacetylation process deprotects the cellulose acetate (CA) to free the hydroxyl group producing cellulose (C) as shown in Figure 3-1. The cellulose acetate nanofibre mats (CANFs) were therefore exposed to 0.05 M NaOH to generate CNFs. Attenuated Total Reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was used to monitor the changes from the difference in chemical composition of the NFs.

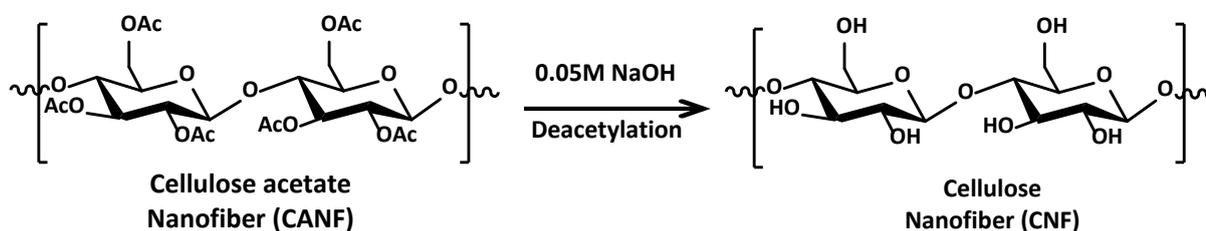


Figure 3-1: Deacetylation of cellulose acetate to cellulose.

3.3.1.2 Cellulose from sugar cane bagasse

Sugar cane bagasse was obtained from the KwaZulu-Natal Province in South Africa, this bagasse was thoroughly dried and kept in a temperature-controlled room to stabilize. This was followed by milling the bagasse into 250-micron sized particles. The process of obtaining cellulose from the raw biomass is described below;

- Dewaxing of raw biomass: The dried areca husk fibres were dewaxed with a (2:1, v/v) mixture of toluene and ethanol for 48 h at 50°C followed by washing with boiling water and dried in air.
- Isolation of cellulose: The bagasse biomass was dried in sunlight and then cut into small pieces. The cut bagasse was milled to become powder. The major parts containing the lignin and hemicelluloses was removed by treating with 5% NaOH solution at a temperature of 50°C for 4 h. The residue of this process was also washed until reach a neutral pH, and it was dried at room temperature for 36 h.
- Preparation of nano-cellulose: The Isolated cellulose from sugarcane bagasse was hydrolyzed with 6 M of 100 mL sulfuric acid with a ratio of cellulose to sulfuric acid 1:20. The hydrolysis of cellulose was carried out in several variations of sulfuric acid concentration, temperature, and time. The hydrolysis process was quenched by adding 10-fold excess distilled water to the reaction mixture. A colloidal suspension produced was centrifuged at 6500 rpm for 30 minutes. Then, it was dialyzed to neutralize the residue and eliminate the sulfate ions until the PH was 7. The resultant fibres were air dried, then further dried in an oven at 40°C overnight.

3.3.2 Grafting poly(-N-isopropylacrylamide) (PNIPAm) onto CNFs for thermoresponsive behaviour.

3.3.2.1 Polymerization of NIPAm

The homopolymerization of NIPAm was achieved via a free radical polymerization reaction carried out in a two-neck round bottom flask with rubber septum in an inert atmosphere as illustrated in Figure 3-2.

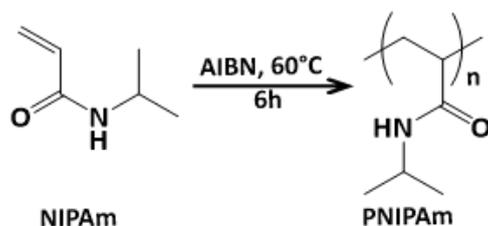


Figure 3-2: Polymerization of NIPAm via free radical polymerization.

3.3.2.2 Grafting of PNIPAm from CNFs

PNIPAm were prepared via free radical polymerization using AIBN as the initiator (Scheme 2). The grafting of the PNIPAm was analyzed by ATR-FTIR (Figure 3-2). Successful formation of PNIPAm on the CNFs was evident by the appearance of peak at 2974 cm^{-1} corresponding to the CH stretch of the isopropyl group. The NH bands at 3386 cm^{-1} is another distinct peak from PNIPAm.

3.3.3 Characterisation of the fabricated nanofibres

Characterisation of the nanofibres was conducted using proton and carbon nuclear magnetic resonance spectroscopy (^1H NMR and ^{13}C NMR), size exclusion chromatography, Fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

3.3.3.1 Chemical characterization by Attenuated Total Reflected-Fourier Transform Infrared (ATR-FTIR)

ATR-FTIR spectroscopy was carried out on a Nexus infrared spectrometer that was equipped with a smart golden gate attenuated total reflectance diamond from Thermo Nicolet with ZnSe lenses. Every sample was scanned 64 times with 4.0 cm^{-1} resolution. The software that was used on the system to do the data analysis was Omnic Software, version 7.2.14.

3.3.3.2 Thermal characterization

- Differential Scanning Calorimetry (DSC) – Differential scanning calorimetry measurements (TA instrument Q100) were conducted under nitrogen atmosphere. The samples (5-10 mg) were sealed in aluminum pans for the measurements. The samples were heated from 10 to 200°C at a rate of $10^\circ\text{C}/\text{min}$, held at 200°C for 1 minute, and cooled at the same rate ($10^\circ\text{C}/\text{min}$), this cycle was repeated twice. The percentage crystallinity of the materials was determined using TA Universal Analysis software version 18.
- Thermal Gravimetric Analysis (TGA) – Thermogravimetric analysis was performed on a Q500 thermogravimetric analyser on nitrogen at $5^\circ\text{C}/\text{min}$. this instrument determines changes in weight in

relation to change in temperature, which translates to the ability of the material to withstand high temperatures. Measurements were performed on 3-5 mg of samples in an aluminium pan under inert N₂ atmosphere with a flow rate of 50 ml/min at a temperature range from 30 to 900°C. 4, 191 mL/min with a pressure of 941 psi

3.3.4 Production and characterisation of the short electrospun fibre sponges

3.3.4.1 *Electrospinning of cellulose nanofibres*

The polymer concentration was 8% (w/v) in trifluoroacetic acid (TFA) solvent. The water and TFA with acetic acid (Merck, Darmstadt, Germany). The polymer solution was then transferred to a 1 mL plastic syringe with a 0.8 mm diameter needle. Flow rate 0.048 mL/min and was controlled by a syringe pump (Kd Scientific, Holliston, MA). A voltage between 12 kV was applied to the polymer solution using a high-voltage power supply. Distance between the needle and the collector plate was 13 cm, and a disk-shaped aluminium plate was used as the collector.

3.3.4.2 *Production of sponges*

A series of CNFs/PNIPAm composite aerogels were fabricated as follows:

Suspensions of PNIPAm modified CNFs (5, 10, 15 and 20% wt/wt) in distilled water were prepared at room temperature ($\pm 20^\circ\text{C}$). The total mass of each sample was fixed at 30 g. Unmodified CNF aerogels (A_0) were also prepared as a negative control as well as a positive control with only PNIPAm (A_5). Each sample was transferred into individual 25 mL beaker and mixed uniformly by magnetic stirring. After that, they were rapidly frozen in liquid nitrogen (-196°C) and then placed in a freeze-drying chamber. The freeze-drying process was maintained at -50°C for 72 h to obtain lightweight sponge-like aerogels with well-defined shape.

3.3.4.3 *Morphological characterization*

- Scanning Electron Microscopy (SEM) -

SEM gives insight about the surface characteristics such as morphology, smoothness, fibre diameter, pore size, and interfibre adhesion properties. Analysis was performed using a Zeiss MERLIN Field Emission Scanning Electron Microscope at the Electron Microbeam Unit of Stellenbosch University's Central Analytical Facility. Prior to imaging, the samples were mounted on aluminum stubs with double sided carbon tape. The samples were then coated with a thin (~ 10 nm thick) layer of gold, using a gold coater for 3 minutes. Scanning electron images of the sample were captured using a Zeiss Secondary Electron (SE2) detector or the Zeiss inlens detector using Zeiss SmartSEM software. The beam conditions during the image analysis were 5 kV acceleration voltage Extra-High Tension (EHT) target, 250 pA beam current (I-Probe), less than 4 mm working distance (WD) and a high resolution column configuration (Column Mode).¹¹ The diameter of the fibres was calculated with AxioVision image analyzer software. Basically, the SEM images were loaded into the software, and the diameter of the fibres was measured using a two-point measuring analysis. Approximately, 50 measurements were taken to obtain the diameter distribution of each type of fibre.

- Transmission Electron Microscopy (TEM)

TEM analysis was performed on a JEOL 1200EX electron microscope operated at 120 kV, at the Electron Microbeam Unit of University of Cape Town's Central Analytical Facility. Samples were prepared by directly depositing nanofibres onto carbon-coated 3 mm diameter copper grids. TEM analysis of nanofibres involves passing the beam of electron that is transmitted through an ultrathin specimen. This technique gives in depth information about the distribution of different additives inside the nanofibre matrix.

3.4 RESULTS AND DISCUSSION

3.4.1 Cellulose extraction

3.4.1.1 Cellulose from cellulose acetate

The effects of polymer concentration and solvent properties on the fibre morphology were then monitored using SEM coupled with EDS. The 15% cellulose acetate solution produced continuous nanofibre (NF) mats with smooth surfaces. While the higher and lower concentrations with different distance displayed formation of droplets with subsequent beading on the fibres. Figure 3-3 illustrates the SEM images of CANFs with smooth and continuous with fibre diameters ranging from 200 to 400 nm and lengths up to several millimetres. Additional variation on the setup parameter will further be investigated, but the smooth fibrous mats were used for further modification.

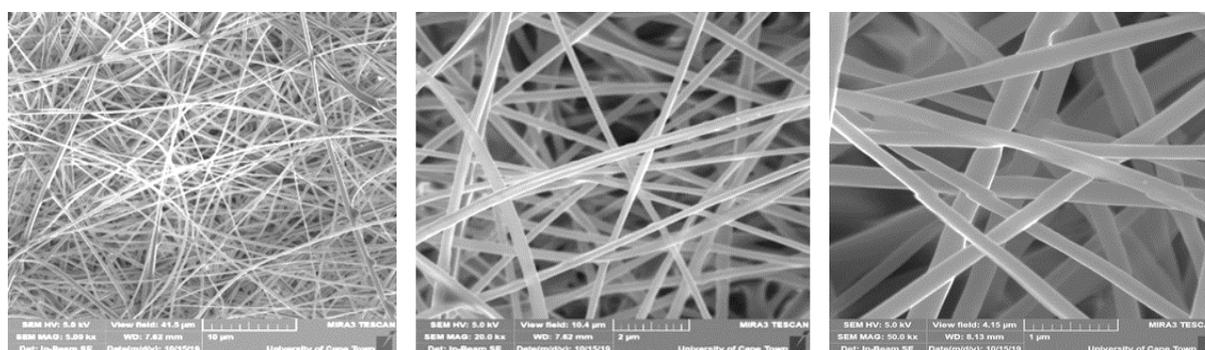


Figure 3-3: SEM images of CANFs.

After alkaline deacetylation, it was evident that the acetyl groups (CH_3CO) were removed (Figure 3-4). A characteristic absorption band at 1750 cm^{-1} corresponding to the removal of ester carbonyls ($\text{C}=\text{O}$). Further disappearance of $-\text{O}$ stretch at 1232 cm^{-1} correspond also to the acetyl functionality indicative of complete deacetylation on the NF mats. The unaffected absorption band due to $\text{C}-\text{O}-\text{C}$ band at $1070\text{--}1000\text{ cm}^{-1}$ is evident that the backbone of the cellulose was retained. The appearance of broad peak at 3340 cm^{-1} is as a result of hydroxyl group further confirming conversion of acetyl to hydroxyl groups.

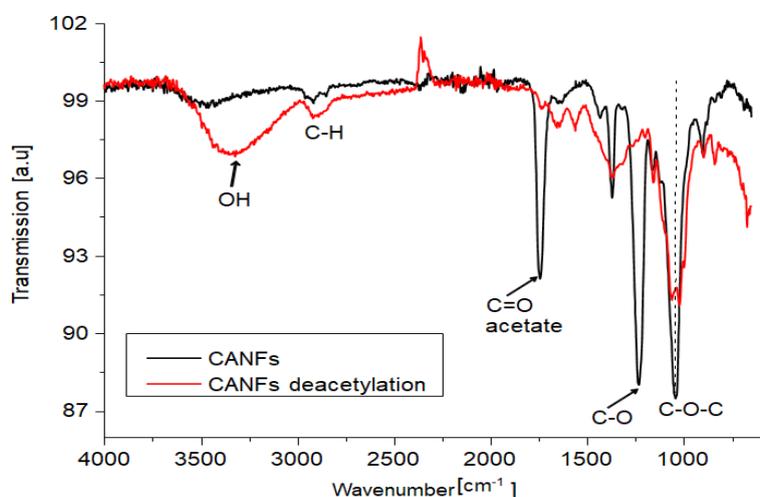


Figure 3-4: FT-IR spectra of cellulose NF mats after deacetylation of CANFs.

For the deacetylation process, two solvents were evaluated, water and ethanol. Ethanol yielded the best fibres and demonstrated fewer finger-like projections compared to the water dispersed counterparts (Figure 3-5). The ethanol dispersed nanofibres also had a lower size variation and minimal bundling compared to water dispersed fibres.

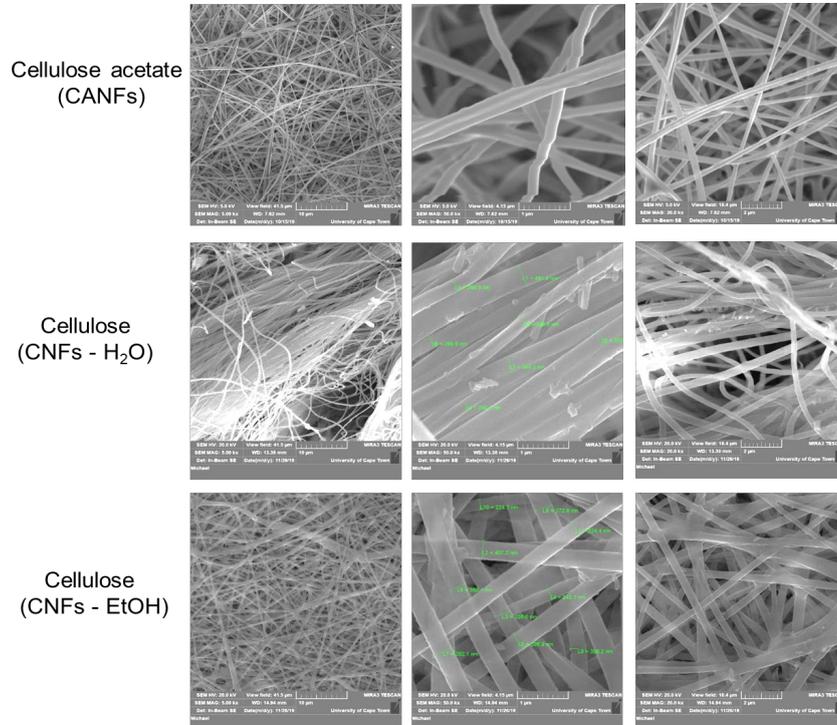


Figure 3-5: CNFs dispersed in different solvents.

From a chemical composition point of view, there were no differences between the fabricated fibres as demonstrated by the ATR-FTIR spectra in Figure 3-6. For the purposes of this study, both types of fibres were suitable for use as short-electrospun fibres.

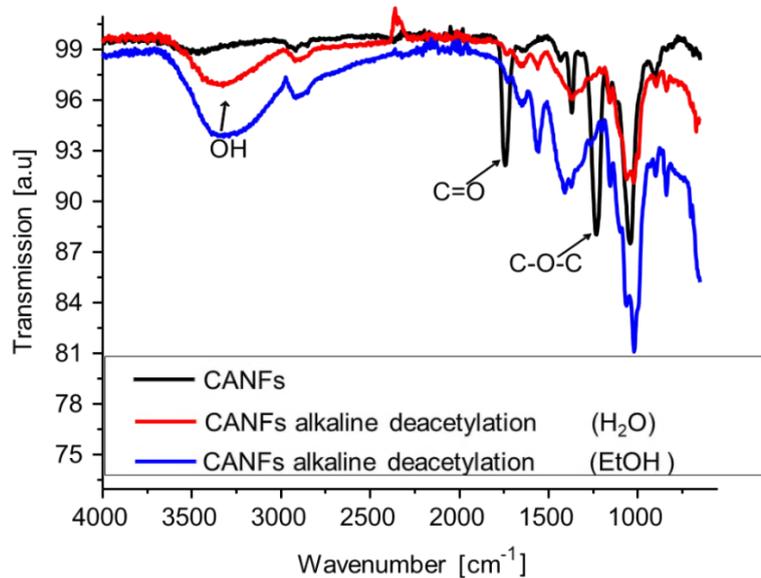


Figure 3-6: FT-IR spectra of cellulose NF mats after deacetylation of CANFs.

The SEM images of the alkaline deacetylation NFs still display smooth surfaces with few small finger-like projections (Figure 3-7). Although the overall process shows insignificant effect on the length of the CNFs. The nanofibres had diameters between 200 nm and 450 nm as indicated in Figure 3-7.

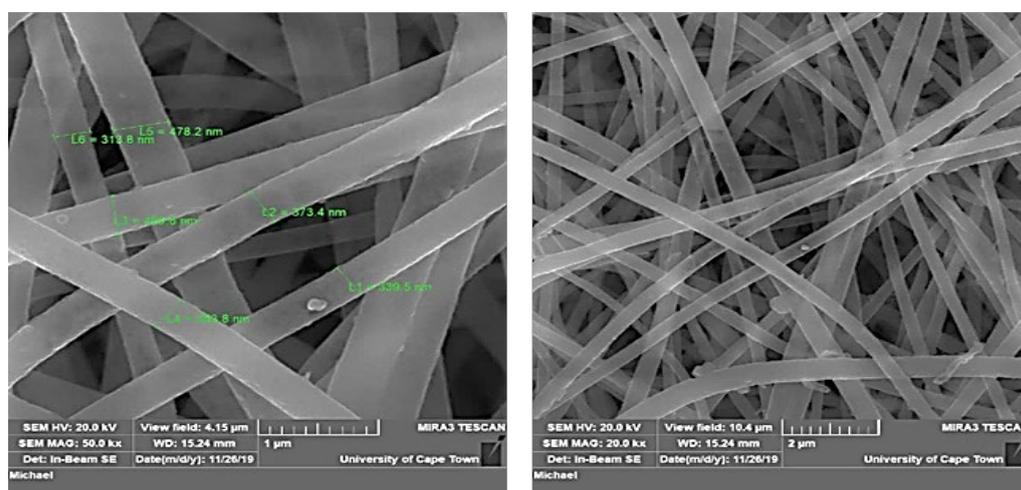


Figure 3-7: SEM images of cellulose nanofibres after deacetylation of cellulose acetate

3.4.1.2 Extraction of cellulose from sugarcane bagasse

Cellulose nanofibrils were extracted from sugarcane bagasse biomass in 3 stages which are dewaxing, isolation of cellulose (removal of lignin and hemicellulose) through alkali treatment and finally the isolation of cellulose nanofibres via acid hydrolysis. Figure 3-8 demonstrates the visual appearance of the progression from raw biomass to cellulose nanofibrils.

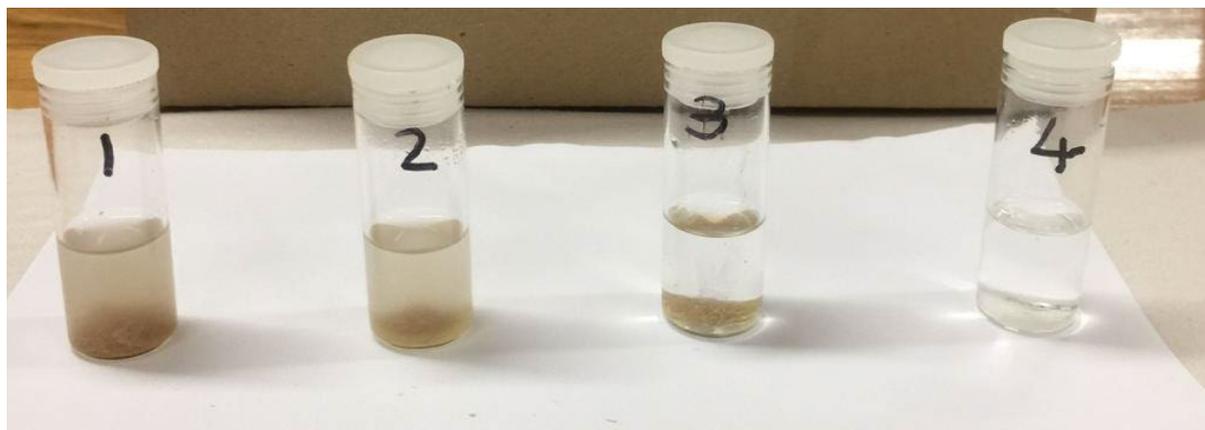


Figure 3-8: Visual image showing the cellulose biomass fibre solutions at different stages of treatment. (1) Raw biomass, (2) Dewaxing, (3) Isolation of cellulose, (4) Isolated cellulose nanofibres

There are two main absorption regions observed for all the fibres (Figure 3-9), one at low wavelength region from 750 to 1750 cm^{-1} and other at high wavelength region between 2800 and 3400 cm^{-1} . The absorption bands in the range 3347-3405 cm^{-1} and 2889-2981 cm^{-1} found in the spectra of all the fibres represent the -O-H stretching vibrations of the hydrogen bonded hydroxyl groups and the CH groups of cellulose respectively. The peaks at 1255, 1507, 1605 cm^{-1} found in the spectrum of raw fibre correspond to the aromatic skeletal vibrations of lignin components. The appearance of a significant peak at 1729 cm^{-1} also in the raw fibre is due to the acetic and uronic ester groups of the hemicelluloses or the ester linkages of the carboxylic group of ferulic and p-coumaric acids of lignin or hemicelluloses. Peaks seen at 1153 and

1094 cm^{-1} are attributed to the C-O-C stretching vibrations of the β -1,4-glycosidic ring linkages between the d-glucose units in cellulose. Additionally, the most significant intense peak around 990 cm^{-1} and a shoulder peak in the region 895 cm^{-1} correspond to the CH glycosidic deformation of cellulose components. In addition, the two sharp signals at 1426 and 897 cm^{-1} reflect the crystalline band of cellulose.

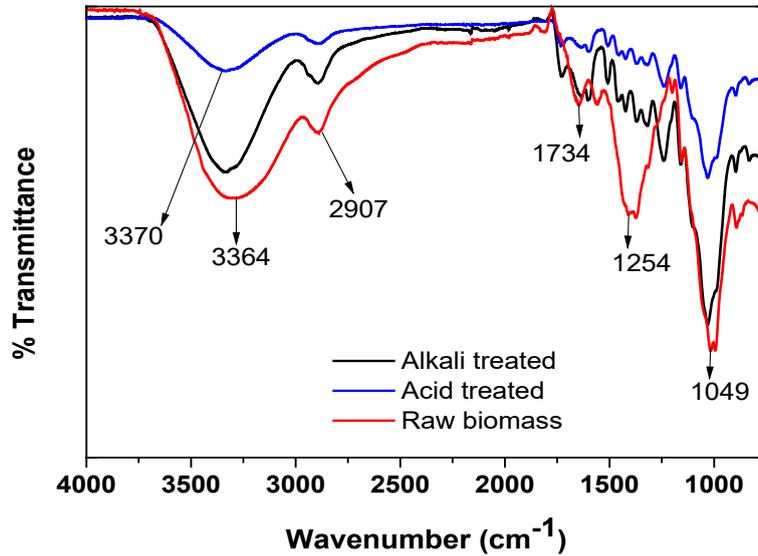


Figure 3-9: FT-IR spectra of fibres at different major stages of processing

3.4.2 Grafting of PNIPAm onto CNFs

Upon grafting, as shown in Figure 3-10, the NH peaks overlap with those of OH with the weak intensity. This overlap is as a result of the hydrogen bonding between the polymer and the CNFs. The CH stretch 2974 cm^{-1} on the NF mat is indicative of successful grafting of PNIPAm. In addition, there is no negative effect of the integrity of the cellulose backbone as the stretching vibration of C=O, and C-O-C groups at 1654 cm^{-1} and 1015 cm^{-1} respectively.

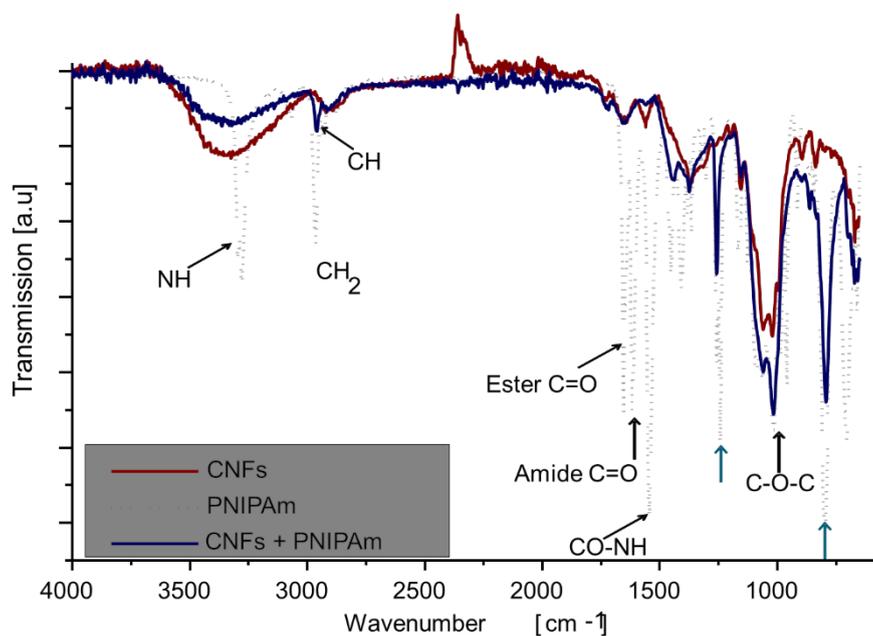


Figure 3-10: FT-IR spectra of cellulose NF mats before and after grafting with PNIPAm.

Thermogravimetric analysis indicated that the degradation of CNFs/PNIPAm occurs in two distinct stages: the initial one at around 315°C being the degradation of the cellulose component, followed by the mass loss associated with the PNIPAm component around 400°C. Unmodified cellulose fibres on the other hand exhibits an onset of degradation around 275°C. This trend was also observed by Zoppe et al., when they studied cellulose nanocrystals decorated with tethered polymer chains of PNIPAm [30]. This behaviour can be attributed to the covalently attached polymers on the surface of the CNFs and subsequently an increase in their thermal stability.

CHAPTER 4: AIR-WATER ABSORPTION AND RELEASE STUDIES

4.1 INTRODUCTION

After the successful preparation of PNIPAm/CNFs sponges, the thermoresponsive capabilities were tested. The thermoresponsive nature of PNIPAm composites is very well reported. And even though very little work has been done on their use to capture water/ moisture, a lot of research has been published in the biomedical field. This phenomenon is well explained by Lanzalaco and Armelin, 2017, at a cloud point, PNIPAm displays a distinctive volume phase transition from a hydrated and expanded state also referred to as the hydrophilic state to a shrunken dehydrated state [3]. The reversibility of the hydrophilic/hydrophobic states occurs by varying the temperature below or above the LCST value (32°C) as illustrated in Figure 4-1.

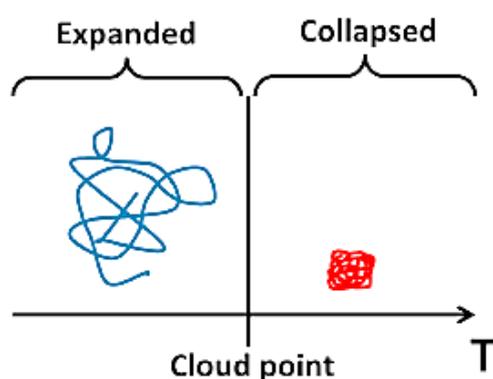


Figure 4-1: Representation of volume phase transition between the expanded (hydrophilic) (left) and the shrinking (hydrophobic) (right) sponge conformations.

4.2 EXPERIMENTAL STUDY DESIGN

Experiments to establish the moisture absorption capacity of the sponges was determined in a controlled laboratory set up and subsequently in an outdoor setup where several aspects are at play (wind, inconsistent temperatures, etc. to give an idea how the sponges would perform in a real-life setting.

4.2.1 Lab scale studies/ simulations

To mimic a real scenario, the system illustrated in Figure 4-2 was set up. This setup comprised of a humidifier, water supply and these were housed inside a temperature-controlled chamber with a glass door. The simulations were carried out at different temperatures and humidity which were monitored using a digital LCD temperature thermometer humidity meter. Various temperatures and humidity combinations were evaluated.

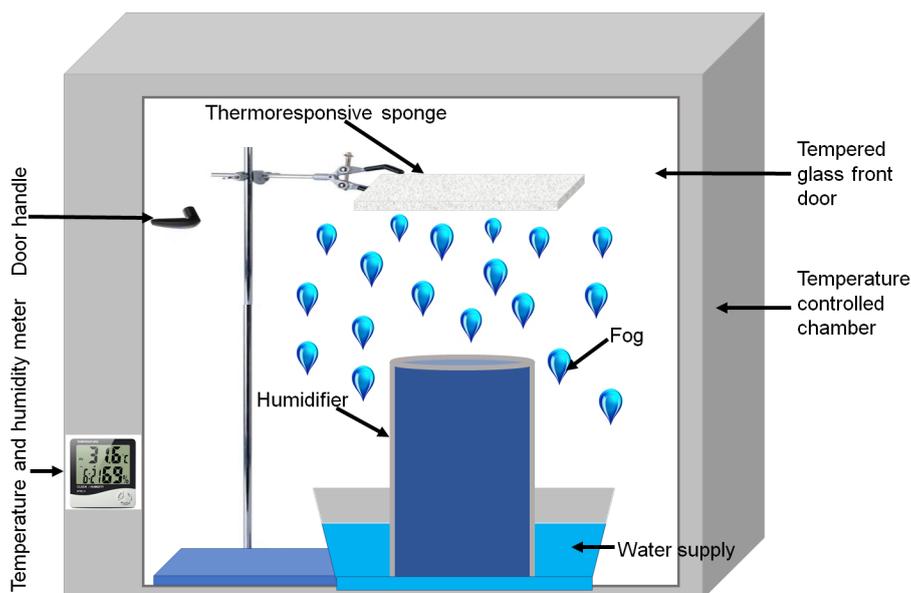


Figure 4-2: Lab scale representation of the air-water capturing experiments.

4.2.2 Outdoor experimental set-up

The outdoor experiments were set up at the balcony of a first floor flat. The humidity and temperature were recorded at the beginning and again at the end of the experiments. The sponges were placed inside aluminium foil pans and these were nicely secured to avoid movement as a result of changing wind conditions. Early in the morning (05h30 South African standard time – GMT+2) (humid and low temperatures) the sponges were weighed, and their original weight was subtracted from the new weight. In the late afternoons (15h00 South African standard time – GMT+2), similar measurements were taken. The amount of water released by the sponges was also recorded. Weather conditions were noted to account for irregularities in the findings. The samples tested included a control sponges (CNFs and PNIPAm) as well as those with varying block ratios of PNIPAm and CNFs.

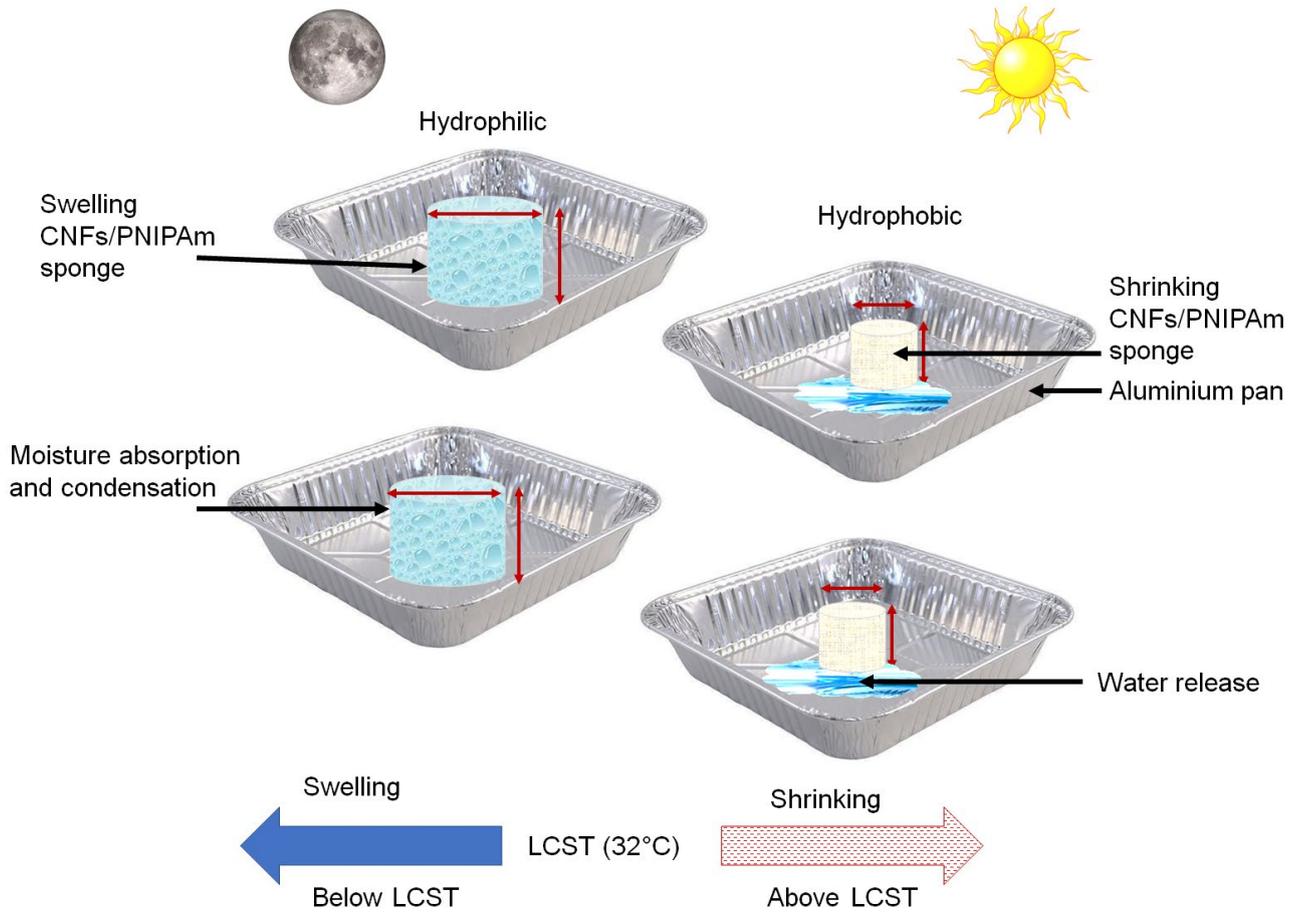


Figure 4-3: An illustration of the outdoor air-water capturing setup.

4.2.3 Moisture absorption studies

The thermoresponsive properties of PNIPAm are well documented. The grafting of PNIPAm onto CNFs was intended to induce this thermoresponsive behaviour to the fabricated materials. The fibres are expected to absorb atmospheric water at low temperatures and release the water above the lower critical solution temperature (LCST) of the thermoresponsive polymers. To establish if this goal was accomplished wettability studies at room temperature *were conducted*. Cellulose nanofibres are frequently regarded as superhydrophilic (super water absorbents), this is because of their high porosity and abundant hydroxyl groups. Water contact angles as well as wettability studies were carried out to determine the effect of PNIPAm modification on the fabricated sponges. *In addition*, air-water absorption and release at different humidity levels and temperatures was studied. The ability of the sponges to absorb atmospheric water was monitored.

4.3 RESULTS AND DISCUSSION

4.3.1 Laboratory scale experiments

The structural integrity of the unmodified CNFs sponge was not stable when the sponge was exposed to water, regardless of the water temperature (20 or 35°C). The CNFs sponge disintegrated into small pieces. Zhang et al., 2016 described this as a consequence of the structure formation of CNFs sponges. The authors stated that the CNFs sponges are constructed through entanglements of CNFs and hydrogen bonds formed between adjacent CNFs which are weak interactions and hence vulnerable in a water environment [32]. Additionally, when the cellulose nanofibre sponges are exposed to water, strong capillary forces are generated in the micropores which destroy the pore structure and consequently the sponges. Sponges A_1 to A_4 however, kept their structural integrity well during contact angle measurements. These sponges demonstrated exceptional temperature responsive water affinity. When evaluated at 35°C the thermoresponsive sponges were hydrophobic with a water contact angles between 90 and 103°. The water droplets retained their structure and were not absorbed by the sponges. In contrary, when the temperature was decreased to 20°C the contact angles were between 0 and 2°. The water droplets were swiftly absorbed by the sponges without any changes in its appearance. Even after leaving the sponges in water at 35°C for 24 h, the sponges floated on the water and the transparency of water did not change. However, when exposed to water at 20°C, the sponges descended rapidly to the bottom of the beaker but still maintained their integrity. These results are summarized in Table 4-1.

Table 4-1: Contact angles and water absorption (WA) of the thermoresponsive sponges

Sample ID	Description	Contact angle		Water absorption (g/g)	
		20°C	35°C	20°C	35°C
A_0	CNFs	N/A	0	N/A	N/A
A_1	5% wt/wt PNIPAm/CNFs	103	0	27.4	2.2
A_2	10% wt/wt PNIPAm/CNFs	97	0	24.7	1.9
A_3	15% wt/wt PNIPAm/CNFs	95	2	19.8	1.5
A_4	20% wt/wt PNIPAm/CNFs	90	2	14.2	0.9
A_5	PNIPAm	-	-	-	-

4.3.2 The effect of temperature and humidity on amount of water absorbed.

Initial investigation on the effect of temperature and humidity on the water absorption capability of the sponges also indicated a decrease in absorbance with increasing temperature which further confirms the strong temperature thermoresponsive nature of the sponges. A similar trend was observed when the sponges were exposed to humid conditions as outlined in Table 4-2.

Table 4-2: The effect of humidity on the amount of water absorbed.

Relative Humidity (%)	Sample ID	Water absorption at 20°C
40	A_0	Sponge disintegrated
	A_1	21.3
	A_2	18.9
	A_3	15.3
	A_4	12.4
	A_5	N/A (sponge melted)
70	A_0	Sponge disintegrated
	A_1	34
	A_2	33.2
	A_3	28.2
	A_4	27.9
	A_5	N/A (sponge melted)

Sponge A_2 (10% wt/wt PNIPAm/CNFs) which demonstrated better absorption in the preliminary results was used for further experiments. Atmospheric water absorption by the sponges was very sensitive to slight temperature and humidity changes as indicated in Figure 4-4 A and B. The most likely explanation this behaviour is a drastic change in the hydrophilicity/ hydrophobicity of the PNIPAm chains above the LCST. From the results obtained, it was also noted that absorption increased with a decrease in temperature and increased with an increase in humidity. This is expected because, at high humidity (%RH), there is more water available for absorption in the atmosphere (air). This trend has been observed by other researchers as well [2, 32].

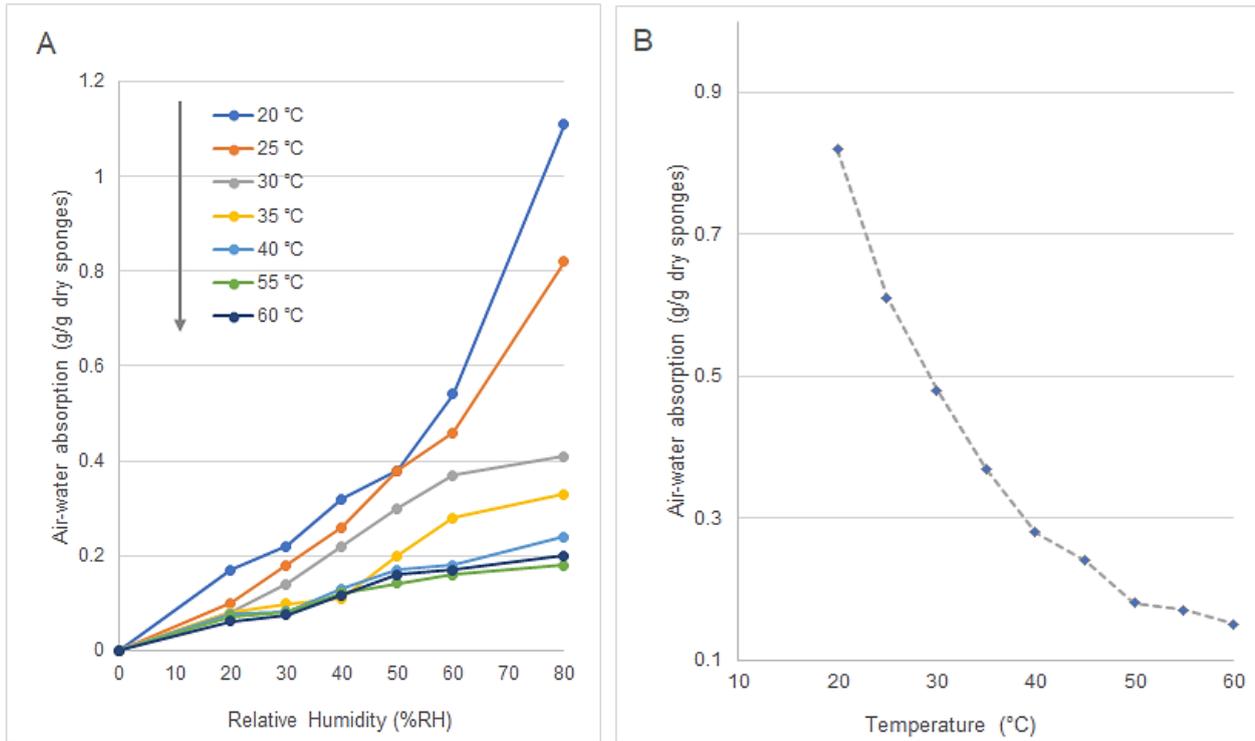


Figure 4-4: Moisture-absorption isotherms of the PNPAm/CNFs sponges at various temperatures (A) The absorption capacity of PNPAm/CNFs sponges at 80% RH and various temperatures.

4.3.3 Recyclability of the sponges

Recyclability analysis was performed over 10 cycled and the amount of water absorbed by the PNIPAm/CNFs sponges at 20°C and 80% RH over 12 hours at a time was statistically similar. These results are demonstrated in Figure 4-5. It is worth noting that the sponge used in these experiments was sponge A_2.

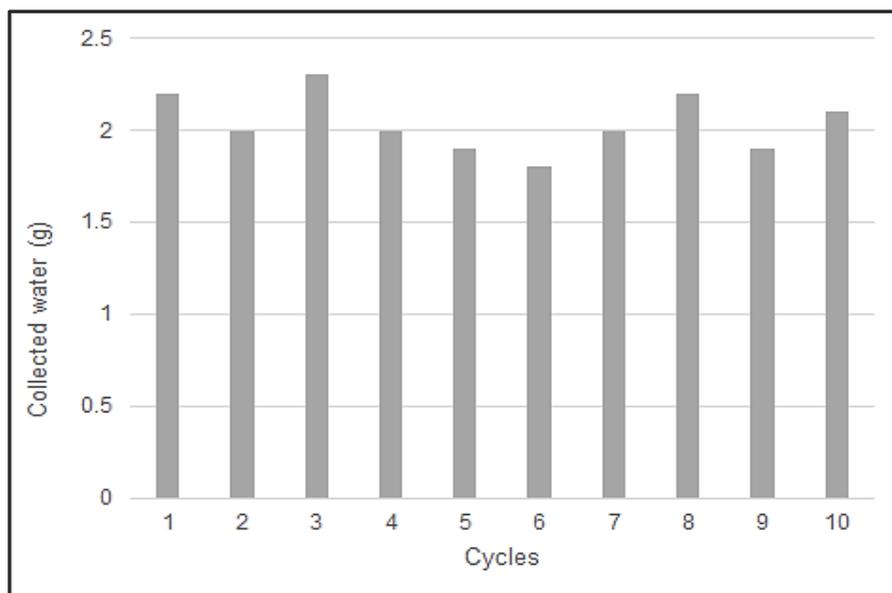


Figure 4-5: Recyclability of the sponges

4.3.4 Outdoor experiment results

Outdoor water absorption also showed a similar trend to that indicated by the laboratory experiments. The overall absorbed water was less than in the simulated experiments. This was as a result of other conditions at play in an outdoor setting as opposed to a controlled setup. For example, wind, fluctuation in temperatures and humidity. The outdoor experiments demonstrated an average air-water absorption of up to 8 times the sponge weight with maximum absorptions of up to 12 times on very humid conditions. These results are outlined in Table 4-3. From the results it is evident that at high humidity and low temperatures, the air-water absorption is enhanced. This was the same trend observed in the laboratory experiments.

Table 4-3: The effect of humidity and temperature on the amount of water absorbed.

Relative Humidity (%)	Average night temperature	Average day temperature	Water absorption average
Below 40	Above 20	Below 20	8.7
40-50	15-20	20-30	12.3
50-60	10-15	30-35	16.1
Above 60	Below 10	Above 35	28.2

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

Cellulose was successfully obtained via two routes (deacetylation of cellulose acetate and extraction from sugarcane bagasse). The cellulose was then modified with PNIPAm to induce thermoresponsive properties. The nanofibre sponges were fabricated via pulverization of the thermoresponsive nanofibres and subsequent lyophilization to obtain sponge-like materials. These sponges have demonstrated excellent thermoresponsive behaviour and Lab scale findings have demonstrated exceptionally positive results with the sponges absorbing up to 15X their weight. The outdoor experiments demonstrated an average air-water absorption of up to 8 times the sponge weight with maximum absorptions of up to 12 times on very humid conditions.

5.2 RECOMMENDATIONS AND FUTURE RESEARCH OUTLOOK

- Synthetic experiments to investigate the produce a full loop system (continuous absorption and release) through the introduction of an upper critical solution temperature (UCST) polymer which can absorb and release water at opposite temperatures proved to be much bigger project than initially expected. An MSc student was appointed to do this part of the project.
- Further work and upscaling of this project needs to be done.
- As a result of promising results in the study: There is an expansion on the project. A collaboration with Dr Luvuyo Tyodha at the University of Stellenbosch, Department of Forestry.
- We will further explore the beneficiation of more waste materials to fabricate sponges for various applications including the cleaning of industrial effluent. The strength demonstrated by the wood products coupled with the capability to chemically modify the OH bonds of cellulose to attach several functional groups which can act as traps for a number of industrial pollutants is very promising. An MSc student has been accepted and will work on this project.
- Wood samples to be included;
 - Soft wood: Pine
 - Hard wood: Eucalyptus
 - Invasive alien species
 - Grass: Bamboo

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