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**New textile structures based in sustainable fibers
spinning**

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Statement of originality

I, Gulnazi Kenzhebay, hereby declare that the work presented in this dissertation, titled "New textile structures based in sustainable fibers spinning," is entirely my own original work. I affirm that it has not been fully or partially submitted previously in any other Italian or foreign university for assessment purposes.

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I understand the consequences of submitting work that is not my own and affirm the honesty and integrity of this academic contribution.

Gulnazi Kenzhebay

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Abstract

The textile industry, a vital component of our global economy, faces mounting challenges regarding its environmental impact within the circular economy framework. To address this issue, this thesis embarks on an exploration of sustainable fiber production methods, aiming to revolutionize eco-friendly practices in the textile industry. The primary objective is to develop fibers from bio-based polymers and proteins, with a dual focus on pioneering innovative manufacturing techniques and ensuring the resulting fibers exhibit exceptional utility in the development of textile products.

Chapter 2 sets the stage by providing a comprehensive overview of the current textile industry landscape, including data on its climate-negative impacts and an exploration of the diverse array of fibers that compose this intricate world. The heart of this research lies in the introduction of sustainable fibers, with a particular emphasis on Chitosan, Collagen, PVA, and the promising PHAs, notably PHB.

The subsequent subchapter delves into the production methodologies used to create these sustainable fibers, such as wet spinning, spraying, and electrospinning. Each method is meticulously examined, as their optimization is crucial for sustainable fiber production.

The Results and Discussion section unveils the findings of the experiments and scrutinizes their implications. This chapter is a culmination of extensive research, blending experimental exploration

with material assessment to discern the mechanical properties of the fibers, including their strength, flexibility, and adaptability across diverse applications in the realm of textile. While the journey is marked by both successes and challenges, each iteration contributes to refining and enhancing subsequent attempts.

In conclusion, this thesis represents both an exploration and a foundation, extending an invitation to venture into uncharted approaches to fiber production in pursuit of environmental sustainability. By introducing pioneering materials and innovative manufacturing techniques, this research seeks to ignite a trajectory of continued research and development. Balancing complexity with accessibility, the narrative shares both achievements and hurdles, aspiring to ignite ideas that propel the textile industry toward a more sustainable and environmentally friendly paradigm.

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List of abbreviations

Abbreviations	Definition
ASTM	American Society for Testing and Materials
cN	Centinewtons
DMF	Dimethylformamide
dtex	Decitex
EDS	Energy Dispersive Spectroscopy
GlcNAc	N-Acetylglucosamine
ISO	International Organization for Standardization
LCL	Long-Chain Length
MCL	Medium-Chain Length
MDL	Minimum Detection Limit
NaOH	Sodium Hydroxide
P3HB	Poly-3-Hydroxybutyrate
PCA	Plate Count Agar
PCMs	Phase-Change Materials
PE	Polyethylene
PET	Polyethylene Terephthalate
PGA	Polyglycolic Acid
PHA	Polyhydroxyalkanoates
PHO	Poly(3-Hydroxyoctanoate)
PHV	Poly(3-Hydroxyvalerate)
PLA	Poly(lactic Acid)

PP	Polypropylene
PVC	Polyvinyl Chloride
SCL	Short-Chain Length
SEM	Scanning Electron Microscope
TE	Tissue Engineering
UV-Vis	Ultraviolet-Visible

Chapter 1. Introduction

Problem Statement

The textile, packaging, and footwear sectors, acknowledged for their substantial contributions to global pollution, present formidable barriers to achieving the European Union's climate neutrality objectives by 2050. Conventional manufacturing processes, characterized by an extensive reliance on non-biodegradable petrochemical-based materials, pose a dual challenge of resource sustainability and environmental integrity. The replacement of fossil raw materials by bio-based ones is crucial for the green transition of manufacturing industries. To lower the environmental impact to a greater degree, bio-based products should be easy to reuse and recycle. CITEVE – The Technological Centre for the Textile and Clothing Industry of Portugal – is involved in several projects in order to expand the use these sustainable materials, decreasing carbon emissions in the textile supply chain. Specifically, Waste2BioComp project, an EU-funded project led by CITEVE, aims to demonstrate relevant scale production of bio-based products and materials, as alternatives to replace traditional materials with a high environmental footprint, using innovative manufacturing technologies in Textiles, Packaging and Footwear. The adaptation and implementation of these progressive solutions within the intricate landscape of the textile sector warrant meticulous examination. Furthermore, the specific niche of sustainable

fibers production using biopolymers, a facet of the broader research, necessitates focused inquiry for comprehensive understanding.

Research Question

This research aims to assess the processing technologies involved and the mechanical properties of the resulting fibers. The study seeks to contribute insights into the viability and environmental impact of utilizing bio-based materials in the quest for more sustainable fiber production. The main research question applied to this study is: "How feasible is the incorporation of innovative bio-based materials in the production of sustainable fibers for the textile industry?" Other questions such as "What are the main spinning techniques to produce fibers and how do they work?" and "What are the targeted properties of bio-based fibers in order to apply them in textile industry?" are addressed during this research work.

Research Within

The specific focus of this research is the production of sustainable fibers using biopolymers within the textile sector. This work was developed at CITEVE – The Technological Centre for the Textile and Clothing Industry of Portugal – located in Vila Nova de Famalicão, during the

period between May and August 2023. CITEVE is a private non-profit organization active since 1989, being a reference organization within the national and European scene, regarding research, innovation, and technology transfer promotion for the Textile & Clothing Industry. CITEVE's mission is to support the technical and technological development of the textile & clothing industry, promoting innovation and inducing new capacities and new competences as well as helping on the definition of industrial public policies. It offers technological services of the highest level in different areas: Laboratorial activities, Technological consultancy & development, R&D+Innovation, Technology Watch, Product standards and certification, Training and Fashion intelligence. Specifically, the current study endeavors to contribute to the broader objectives of the Waste2BioComp project by exploring novel methods and optimizing manufacturing processes for the synthesis of these fibers. By concentrating on the development and adaptation of biopolymers for fiber production, this research aspires to play a pivotal role in reshaping the textile industry towards sustainability. The inquiry into sustainable fibers production serves as a microcosm within the larger framework of the Waste2BioComp initiative, aligning with the overarching mission of achieving climate neutrality by 2050.

Objective

This thesis endeavors to explore different methodologies for sustainable fiber production, aiming to contribute to the evolution of eco-friendly

practices within the textile industry. The primary objective is to develop fibers utilizing bio-based polymers and proteins, with a dual emphasis on manufacturing techniques and ensuring that the resultant fibers exhibit superior utility in textile products manufacturing.

The research delves into the intricacies of protein-based fibers, leveraging these biopolymers as building blocks for sustainable material development. The focus lies not only on the synthesis process but also on the thorough evaluation of the mechanical properties—seeking to understand the strength, flexibility, and versatility of these fibers for diverse applications in the realm of the textile industry, in particular for high-value applications like medical textiles.

In tandem with material exploration, the study systematically tests 2 manufacturing methods (spraying and dry-jet wet spinning techniques), aiming to optimize the production process. While certain methodologies may yield unexpected results, each iteration serves as a valuable learning experience. Failures are meticulously documented and analyzed, providing insights that contribute to the refinement and enhancement of subsequent attempts.

This thesis serves as both an exploration and a foundation—a call to delve into unprecedented approaches to fiber production in pursuit of

environmental sustainability. Through the introduction of pioneering materials and differentiating manufacturing techniques, this research aspires to inspire a trajectory of continued research and development. Balancing complexity with accessibility, the narrative shares both successes and challenges, aspiring to kindle ideas that propel the textile industry towards a more sustainable and environmentally friendly paradigm.

Chapter 2. Literature Review

Contextualizing the textile industry and its environmental impact

In the year 2020, the environmental and climate change impact of textile consumption in Europe was shown to be the fourth highest globally, as assessed from a life cycle viewpoint. This textile consumption sector showed the third most significant influence on water and land utilization, while ranking fifth in terms of raw material use and greenhouse gas emissions (European Environment Agency, 2022). According to estimates of European Environment Agency, the fashion business is accountable for approximately 10% of worldwide carbon emissions, surpassing the combined emissions of international aircraft and maritime shipping. The European Environment Agency (2023) also determined that the average textile consumption per individual in the European Union (EU) during the year 2020 needed approximately 400 square metres of land, 391 kg of raw materials, and 9 cubic metres of water. The whole carbon footprint amounts to approximately 270 kilogrammes (European Parliament, 2023). According to the Ellen MacArthur Foundation, it is projected that the fashion sector will deplete around 25% of the global carbon budget by the year 2050. Moreover, if the current linear and wasteful supply chain is maintained, industry will consume more than

26% of the carbon budget by 2050 (Ellen MacArthur Foundation, Fashion and circular economy n.d.)

To mitigate the adverse impacts of the fashion industry on sustainability, the implementation of circular economy approaches is necessary. Circular economy is an economic model that aims to minimize waste and maximize the use of resources by keeping products and materials in use for as long as possible (Gardetti, 2019), (Ellen MacArthur Foundation, Circular economy introduction n.d.).

In the context of the textile industry, this can involve practices such as recycling, upcycling, and designing products for durability and easy disassembly. By transitioning from a linear and wasteful supply chain to a circular economy model, the industry can reduce its environmental impact and promote sustainability. For example, instead of discarding textile waste, it can be recycled into new fibers or used in other industries, reducing the need for virgin resources, and minimizing waste (Manickam & Duraisamy, 2019).

The present state of the fashion, garment, and textile sectors raises concerns from a sustainability standpoint. A significant proportion of the raw materials utilized, and the final products (including fibers and clothes) manufactured have adverse environmental impacts. The concept of "fast fashion" refers to a phenomenon characterized by the reduction in the lifespan of products and the accelerated influx of textile items into the environment. Based on current estimations, non-biodegradable synthetic fibers have emerged as the predominant choice in fiber

production, despite their inherent potential for recycling and reutilization due to their unique chemical compositions (Moorhouse & Moorhouse, 2017).

The production of textiles is characterized by a series of intricate processes, from raw material cultivation to manufacturing and finishing. Each stage leaves an indelible mark on the environment. Cotton, a predominant textile fiber, exemplifies this impact. The extensive use of water, pesticides, and energy in cotton farming contributes to soil degradation and water pollution, while manufacturing processes, such as dyeing and finishing, release pollutants into the air and water. One of the primary obstacles to achieving sustainability lies in the significant water consumption and pollution associated with textile wet processing operations, including dyeing, finishing, sizing, and similar procedures (European Commission, 2023).

In 2021, there was a significant increase in global fiber output, reaching an unprecedented 113 million tonnes. This positive trend follows a minor setback in 2020, primarily attributed to the impact of the COVID-19 pandemic. Over the past two decades, there has been a significant increase in worldwide fiber output, with a nearly twofold rise from 58 million tonnes in 2000 to 113 million tonnes in 2021. Projections indicate that this upward trend is likely to persist, with an estimated growth to 149 million tonnes by 2030 under the assumption of business as usual (“Preferred Fiber and Materials Market Report”, 2023).

The environmental impact of consumer use is significant, mostly due to the consumption of water, electricity, and chemicals during the processes of washing, tumble-drying, and ironing. Additionally, the shedding of microplastics into the environment further contributes to this footprint. Only half of utilized garments are procured for the purpose of reuse or recycling upon reaching the end of their usefulness. Furthermore, a mere 1% of these garments undergo recycling processes to be transformed into new clothing items. This limited rate of recycling can be attributed to the still developing technologies that facilitate the conversion of used clothes into fresh fibers (“Textiles and the Environment”, 2022).

There are two primary categories of textile fiber commonly employed in the production of clothing: natural fibers and synthetic fibers. Natural fibers encompass a variety of materials that are derived from natural sources, such as cotton, wool, sisal, silk, and other comparable substances. In contrast, synthetic fibers comprise materials like polyester, nylon, acrylic, and other analogous substances, which are artificially produced. Based on the findings of the Preferred Fiber and Materials Market Report, it is evident that the worldwide fiber market in the year 2021 was primarily dominated by Synthetic Fibers, constituting approximately 64% of the market share. Plant Fibers followed closely behind, accounting for around 28% of the market. Manmade Cellulosics and Animal Fibers held smaller portions of the market, representing approximately 6% and 2% respectively (“Preferred Fiber and Materials Market Report”, 2023).

Based on estimations, it is projected that synthetic fibers will constitute approximately 98% of all forthcoming fibers, with polyester accounting for approximately 95% of this proportion (Chen et al., 2021). The rise of synthetic materials has generated environmental concerns due to a multitude of issues from many perspectives. According to Gardetti (2019), it is projected that the global manufacturing of synthetic polymers, which have direct applications as fibers, dyes, and finishes, will consume around 98 million tonnes of oil per year. Additionally, it is important to note that synthetic fibers lack the ability to undergo biological decomposition. These entities have the capacity to persist in the surrounding environment for an extended duration. Moreover, fibers provide a greater risk compared to centimeter-scale polymers because to their tiny nature, measuring in the micron range.

As an illustration, the frequent laundering of synthetic garments results in the discharge of nano and microfibers into aquatic environments, hence causing detrimental effects on marine organisms and crucial ecosystems. The intricate nature of these impacts makes it challenging to accurately track their origins (European Environment Agency, 2022). Another important point is resource depletion and waste generation, which is a dual challenge. Resource depletion is a critical concern associated with textile production. The demand for vast quantities of water, coupled with the cultivation of resource-intensive crops, places a strain on ecosystems. Concurrently, the generation of textile waste, including offcuts and end-

of-life products, contributes to landfill overflows (European Environment Agency, 2023).

Types of polymers and fibers in the textile industry

The textile industry, a vast and dynamic realm at the intersection of science, technology, design and art, relies fundamentally on the selection and manipulation of polymers and fibers. These foundational elements dictate the fabric's strength, texture, and overall performance. This section embarks on a comprehensive exploration of the diverse landscape of polymers and fibers employed within the textile industry. Delving into this intricate tapestry, the nuances of materials unfold, forming the very fabric of our daily lives and shaping the clothes we wear, as well as the textiles that surround us.

Textile polymers, the molecular building blocks of fibers, encompass a spectrum ranging from naturally occurring to synthetically engineered. Natural polymers, such as cotton and silk, have been woven into the fabric of human history for centuries, embodying traditions and cultures (Karimah et al., 2021). Conversely, the advent of synthetic polymers, exemplified by polyester and nylon, has revolutionized industry, offering enhanced durability and versatility (Laning, 1992).

The exploration of textile polymers commences with an in-depth analysis of the complex molecular structures inherent in natural fibers. A fundamental understanding of these polymers is essential for unraveling

the complexities that govern their unique properties and applications. Natural fibers, characterized by their biogenic origin, exhibit a diverse range of molecular structures (Karimah et al., 2021). Cellulosic fibers, such as cotton, derive from the cellulose component in plant cell walls, presenting a linear polymer structure comprised of glucose units (European Commission, 2023). This structural arrangement endows cellulose with desirable attributes, including breathability, absorbency, and comfort in textile applications. Protein-based fibers, exemplified by wool and silk, boast complex molecular structures. Wool fibers consist primarily of keratin proteins, characterized by a helical conformation that contributes to the fiber's elasticity and resilience (European Commission, 2023). Silk fibers, produced by silkworms, feature fibroin proteins organized in a beta-sheet structure, endowing silk with remarkable tensile strength and smooth texture (Jin et al., 2022). The molecular diversity within natural polymers extends to fibers sourced from minerals, such as asbestos, a naturally occurring silicate mineral. Although the use of asbestos in textiles has diminished due to health concerns, its fibrous nature stems from a crystal lattice structure that imparts strength and fire-resistant properties. In the realm of natural polymers, the interplay of molecular structures dictates the distinct characteristics of each fiber, influencing factors such as strength, flexibility, and thermal properties (Karimah et al., 2021). The scientific investigation of these molecular

compositions serves as a foundation for understanding the intrinsic qualities that render natural fibers invaluable in textile applications.

The basic unit of textile structures is fibers. Fibers, the result of polymer processing, exhibit a myriad of forms and characteristics. Staple fibers, short in length and often natural, are spun together to create yarns with a distinct texture. In contrast, continuous filament fibers, extruded in long strands, contribute to fabrics with a smoother finish and increased strength (Kadolph, 2013). The interplay between these fiber types shapes the textile landscape, determining the feel and functionality of the final product. Table 1 shows the classification of textile fibers, divided in natural and man-made origin.

Table 1. General classification of fibers (European Comission, 2023)

Natural origin fibers	Animal origin	Raw wool Silk fiber Hair
	Vegetable origin	Raw cotton fiber Flax Jute
Chemical fibers (man-made)	Natural polymer fibers/ Man-made cellulosic fibers (MMCF)	Viscose, Cupro, Lyocell Acetate Triacetate

	Synthetic polymer fibers	Organic polymer	Polyester Polyamide Acrylic Polypropylene Elastane
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Introduction to sustainable polymers and fibers

Sustainable polymers are materials that can be recycled, biodegraded, or composted at the end of their useful lives and are made from renewable, recycled, and waste carbon resources (Mohanty et al., 2022). Sustainable polymers have also a lower overall environmental impact throughout their lifetime. New sustainable polymers, though still in their infancy, are already being used in 3D printing, packaging, and automotive parts (Mohanty et al., 2022). By decreasing the production and use of virgin plastics made from finite resources, the development of sustainable polymers will hasten the age of sustainable polymers and establish a true circular economy for plastics (Mohanty et al. 2022). A sustainable polymer, also known as an eco-friendly or green polymer, refers to a polymer that is produced and utilized in a manner that minimizes its environmental impact throughout its entire life cycle (Mohanty et al. 2022). Sustainable fibers take a holistic approach to the topic of sustainable textiles, starting with the production of the fiber and

continuing through to manufacturing, low-energy maintenance, and recycling (Muthu, 2016). Sustainability in polymers involves considerations from the extraction or synthesis of raw materials, the manufacturing process, product use, and eventual disposal or recycling (Muthu, 2016). As per the research conducted by Mohanty et al. (2022), the fundamental attributes of sustainable polymers encompass:

1. **Raw Material Source:** Sustainable polymers often use raw materials derived from renewable resources, such as plant-based feedstocks like cornstarch or sugarcane, as opposed to fossil fuels;
2. **Biodegradability:** Some sustainable polymers are designed to be biodegradable, meaning they can break down into natural substances when exposed to environmental conditions, reducing the persistence of plastic waste;
3. **Recyclability:** The ability to recycle polymers is crucial for sustainability. Recyclable polymers can be reprocessed into new products, reducing the demand for new raw materials and minimizing waste;
4. **Reduced Energy Consumption:** Sustainable polymer production methods aim to minimize energy consumption, greenhouse gas emissions, and other environmental impacts associated with traditional polymer manufacturing processes;

5. Non-Toxicity: Sustainable polymers are often designed to be non-toxic and safe for use in various applications, reducing potential harm to human health and the environment;

6. Life Cycle Assessment (LCA): The sustainability of a polymer is often assessed through a life cycle analysis, considering environmental impacts from the extraction of raw materials to the end-of-life disposal or recycling.

Examples of sustainable polymers include polymers as Polylactic Acid (PLA), Polyhydroxyalkanoates (PHA); Polyethylene Terephthalate (PET) from Recycled Sources; etc.

The sustainable raw materials studied during current work are described below.

Chitosan

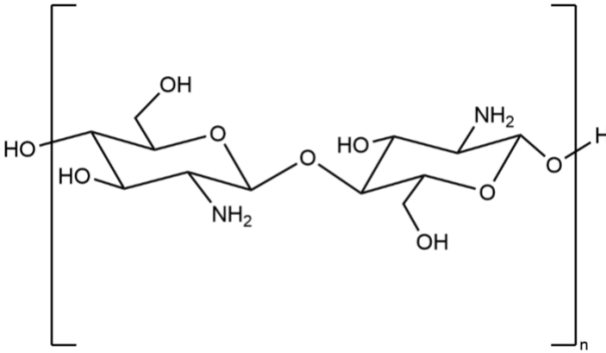


Figure 1. Chemical structure of chitosan

Chitin is the second most available polysaccharide on earth after cellulose. It is obtained on an industrial scale from various sources of biomass and food waste, such as the exoskeletons of crustaceans and insects, fungal cell walls, and squid pens. Chitin is deacetylated to produce chitosan, i.e., a linear polyamine with reactive amino and hydroxyl groups. Many transition metal ions are chelated by it. Rouget discovered the polysaccharide biopolymer chitosan in 1859, and it is now known as the "Million Dollar Natural Polymer." Chemically, it is made up of units of glucosamine and N-acetylglucosamine that are joined together by one-fourth of glucosidic bonds (Shirvan et al., 2022).

Chitosan, exhibits water solubility under acidic conditions and has found applications in numerous industries, including biomedical, pharmaceutical, agriculture, and food. However, a major challenge in the broader adoption of chitosan is the difficulty in accurately characterizing samples. This includes determining the quantities and distribution of

acetyl groups along the chains, the distribution of molecular weights, and the choice of a suitable solvent for dissolution. This knowledge is essential for selecting an appropriate chitosan for specific functions. Another significant concern is the development of well-defined derivatives through chemical methods, enabling the creation of polymers with consistent properties for specific applications (Rinaldo & Goycoolea, 2019).

Research on chitin and chitosan has led to the creation of innovative biomaterials, including films, fibers, nanoparticles, composite materials (involving fibers, solid particles, etc.), hydrogels, polymeric complexes, nanoporous scaffolds, and membranes. These materials have a wide range of applications, such as scaffold biomaterials used in tissue engineering and regenerative medicine, non-viral gene delivery systems, nano- and microparticles for transmucosal biological delivery, coatings for fruits and vegetables, biosensors, matrices for water purification, and new antimicrobial agents (Rinaudo & Goycoolea, 2019).

To provide textiles an antistatic and soil release finish, chitin derivatives have been used. Chitosan has the ability to remove dyes from discharge water, while chitin is used in printing and finishing preparations. Both have made a noteworthy contribution to textile sutures, threads, and fibers used in the medical field.

Numerous endeavors have been made to fabricate chitin and chitosan fibers by the wet spinning technique, with the aim of utilizing them in biomedical applications. The manufacturing circumstances have a considerable impact on the final quality of the fibers. In order to produce wet-spun chitin and chitosan fibers, the utilization of a strong polar solvent is required to disrupt the hydrogen bonding and facilitate the dissolution of the molecules. Subsequently, an appropriate coagulant is employed to induce the recrystallization process (Wang et al., 2020). Wet-spun biomaterials of this nature are commonly employed in drug delivery applications and the fabrication of sutures. The work by Shirvan et al. (2022) employed wet spinning as a method to fabricate chitosan and N-acetyl-D-glucosamine (GlcNAc)-loaded chitosan filaments, which exhibited a core-sheath smooth structure. The obtained findings indicated that the wet-spun structure composed of chitosan exhibited favorable characteristics for the production of absorbable surgical sutures. These characteristics include biodegradability, biocompatibility, as well as sustained and extended release of drugs (Shirvan et al., 2022).

Polyvinyl Alcohol

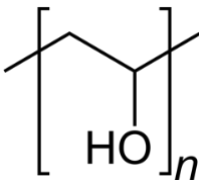


Figure 2. Chemical structure of Polyvinyl Alcohol

In 1924, Hermann and Haehnel pioneered their synthesis through the saponification of poly(vinyl ester) with a sodium hydroxide solution, resulting in a PVA solution (Ben Halima, 2016) . The physicochemical and mechanical properties of PVA are primarily determined by the number of hydroxyl groups within the PVA polymer (Eagland et al., 1986). It is worth noting that PVA is not synthesized through the direct polymerization of its structural monomer, vinyl alcohol, due to its inherent instability. In the commercial production of PVA, vinyl acetate is used as the fundamental raw material for the polymerization process. Controlled partial alkaline hydrolysis, also known as saponification, is carried out on vinyl acetate, where the ester group is partially substituted with hydroxyl groups in the presence of an aqueous sodium hydroxide solution. The resulting product of this reaction is known as PVA.

Commercial production of polyvinyl acetate typically occurs through a continuous process. The hydrolysis of acetate groups occurs by ester exchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide. The physical features and particular functional applications of a substance are contingent upon the extent of polymerization and hydrolysis. Polyvinyl alcohol may be categorized into two distinct classes: partly hydrolyzed and fully hydrolyzed. Partially hydrolyzed PVA is utilized in the food industry. (Rigved et al., 2019)

PVA is a colorless and odorless substance that exhibits translucency. It is typically found in the form of a white or cream-colored granular powder. PVA holds significant commercial value, particularly in applications involving water. The substance exhibits solubility in water, displaying modest solubility in ethanol, while remaining insoluble in several other organic solvents.

PVA finds widespread use in the field of biomedicine due to its compatibility. PVA composites, such as PVA gels, are employed in various biomedical applications, including the development of contact lenses (Hyon et al., 1994), artificial heart surgery (Jiang et al., 2004), drug delivery systems (Kayal & Ramanujan, 2010), and wound dressings (Kokabi et al., 2007).

PVA has a diverse range of applications beyond biomedicine, spanning molecular sensing in biological and biomedical domains, fuel cell membranes, chemosensors, the absorption of toxic metals, and optoelectronic devices. The key concept behind enhancing the properties of polymeric nanomaterials is the increased specific surface area provided by nanofillers, facilitating interaction with the polymer. In the realm of medical devices, PVA serves as a valuable biomaterial due to its highly promising characteristics, including biocompatibility, non-toxicity, non-carcinogenic nature, swelling properties, and bio adhesive features. These qualities make it highly sought after for biomedical applications.

The exceptional mechanical properties of PVA nanocomposites are designed with the intention of being environmentally friendly, as they can be composted at the end of their lifecycle instead of ending up in landfills, in contrast to most traditional petroleum-based non-biodegradable plastics. This approach is particularly relevant in the context of orthopedic applications, as demonstrated in the fabrication and characterization of PVA/TiO₂ nanocomposite films (Mohanapriya & Raj, 2018) and PVA/amino acid composites (Mohanapriya et al., 2016).

In the context to the Waste2Biocomp EU project, polyhydroxyalkanoates (PHA) and polyhydroxybutyrate (PHB) are being studied.

Polyhydroxyalkanoates

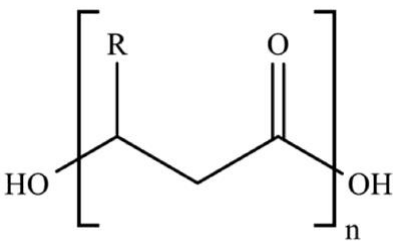


Figure 3. Chemical structure of Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHA) are a class of biopolyesters that are synthesized by a range of microorganisms in their natural environment.

PHAs, initially identified by Lemogine in 1926 (Anderson & Dawes, 1990), have garnered significant attention from both commercial and scientific sectors owing to their notable characteristics such as biodegradability, biocompatibility, chemical variety, and ability to be produced from renewable carbon resources (Shah et al., 2008). PHA molecules are commonly composed by a range of 600 to 35,000 monomer units of (R)-hydroxy fatty acid (Khanna & Srivastava, 2005). The monomer unit has a side chain R group, often a saturated alkyl group. However, it is also possible for the R group to be an unsaturated alkyl group, a branched alkyl group, or a substituted alkyl group, but these variations are less frequently observed (Lu et al., 2009). PHA may be categorized into three types based on the number of carbon atoms present in a PHA monomer: short-chain length PHA (scl-PHA; 3 to 5 carbon atoms), medium-chain length PHA (mcl-PHA; 6 to 14 carbon atoms), and long-chain length PHA (lcl-PHA; 15 or more carbon atoms) (Tan et al., 2014).

The majority of commercially accessible PHAs are derived from pure microbial cultures that are cultivated on renewable feedstocks, such as glucose, in a sterile environment. However, recent research efforts have been directed towards investigating the utilization of waste materials as growth media for PHA production. PHAs can be obtained from bacterial cells and subsequently processed through extrusion techniques to produce both rigid and flexible plastics. These plastics have been found to be suitable not only for various medical applications that have been extensively evaluated, but also for a wide range of other applications such

as packaging, mold goods, paper coatings, non-woven fabrics, adhesives, films, and performance additives (Bugnicourt et al., 2014).

PHAs are microbial storage materials that are formed by various prokaryotes. These materials have shown promise as potential alternatives to conventional plastics in several industry areas, including packaging and biomedical applications. It is crucial to note that the complete production cycle of PHAs, which includes the identification of resilient production strains, selection of suitable feedstock, implementation of fermentation technology, engineering of the process, design of bioreactors, and the subsequent downstream processing, must adhere to sustainability standards (Koller, 2017). PHAs are commonly synthesized by various prokaryotes as intracellular inclusion bodies. These high-molecular compounds serve as storage materials for carbon and energy. They play a crucial role in enhancing the survival capabilities of cells during unfavorable environmental conditions, such as nutrient scarcity or exposure to external stressors. By acting as secondary metabolites, PHAs contribute to the fitness and resilience of cells during periods of famine and stress. From a technological perspective, PHAs possess characteristics that make them suitable for replacing conventional plastics in various sectors of the plastic market. These characteristics include being bio-based, bio-synthesized, bio-compatible, and bio-degradable. PHAs show particular promise in the packaging industry, but also hold potential in niche areas like the biomedical field (Koller, 2017).

Nevertheless, the issue in producing fibers from PHAs lies in their high crystallinity and narrow processing window, as the thermal degradation temperature closely approaches the thermal breakdown temperature. Short-chain length polyhydroxyalkanoates (PHA), such as poly-3-hydroxybutyrate (P3HB) or poly(3-hydroxyvalerate) (PHV), exhibit thermoplastic characteristics characterized by elevated melting temperatures. These PHAs are highly crystalline, rigid, and prone to brittleness (Puppi et al., 2019). On the other hand, medium-chain length PHAs (mcl-PHAs), such as poly(3-hydroxyoctanoate) (PHO), possess an elastomeric nature, displaying low tensile strength and high elongation at break. Additionally, mcl-PHAs exhibit lower crystallinity and a reduced glass transition temperature when compared to short-chain length PHAs (scl-PHAs). The inherent characteristics of mcl-PHAs render them highly appropriate for a wide range of medical applications, including but not limited to cardio-vascular grafts (Williams et al., 1999), artificial esophagus (Chen & Wu, 2005), and tendons or ligaments (Chen & Wu, 2005) where the presence of elastic biomaterials is essential (Kopf et al., 2022).

PHAs have been subjected to comparison with polypropylene (PP) due to their analogous characteristics, including their ability to provide effective resistance against moisture and scent barrier capabilities (Bugnicourt et al., 2014). Many PHA-based textiles exhibit natural odor resistance due to their biocompatible nature. This feature is valuable in sportswear where odors can be a concern. Moreover, this means that PHA fibers can

provide moisture-wicking properties, contributing to comfortable activewear and sportswear. The features of PHAs encompass favorable UV resistance, non-toxicity, water insolubility, and limited tolerance to both acidic and basic environments (Bugnicourt et al., 2014).

The incorporation of PHA with other polymeric or natural raw materials has been widely regarded as a highly effective approach to enhance its qualities. According to Li et al. (2016), The use of cellulose derivatives as blending agents with PHA has gained considerable attention, principally owing to their compatibility with PHA and their capacity to augment the degrading process of PHA.

Polyhydroxybutyrate

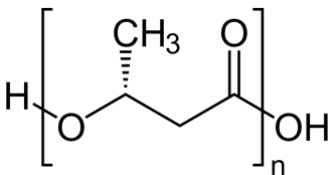


Figure 4. Chemical structure of Polyhydroxybutyrate

Polyhydroxybutyrate (PHB) is a kind of biopolymer that has garnered significant attention in the field of biotechnology. Among the several polyhydroxyalkanoates (PHAs), poly(3-hydroxybutyrate) (P3HB) has

the distinction of being the first to be identified and thoroughly studied. P3HB has a high degree of crystallinity as a result of its linear chain configuration, which encompasses both amorphous and crystalline regions (McAdam et al., 2020). P3(HB) has many benefits compared to synthetic polymers in the context of certain packaging applications. Notably, P3(HB) demonstrates improved barrier permeability in comparison to both polyethylene (PE) and polypropylene (PP) (McAdam et al., 2020). Additionally, P3(HB) exhibits greater rigidity and reduced flexibility when compared to PP (McAdam et al., 2020). In addition, it has been shown that PHB demonstrates superior barrier qualities when compared to polyethylene terephthalate (PET) and polyvinylchloride (PVC) (Markl, 2018). One additional prominent attribute of the P3(HB) material is its capacity for biodegradation, which takes place within a reasonable timeframe when the material comes into contact with degrading microorganisms in biologically active settings such as soils, fresh water, and both aerobic and anaerobic composting. This characteristic positions P3(HB) as a highly desirable environmentally friendly substitute for synthetic polymers (Brandl et al., 1988).

However, the primary concern associated with PHB is its fragility resulting from its extremely crystalline structure. The investigation of brittleness and cracking in PHB was initially conducted by Barham and Keller in 1986 (Barham & Keller, 1986). El-Hadi et al. (2002) conducted a study to investigate the relationship between crystallinity, morphology, and mechanical characteristics of PHB (El-Hadi et al., 2002). The

researchers discovered a correlation between smaller spherulites and enhanced mechanical performances. In a study conducted by El-Hadi in 2014, the non-isothermal crystallization behavior of PHB was investigated in the presence of nanoclay (Mohamed El-Hadi, 2014). The inclusion of nanoclay was shown to induce heterogeneous nucleation, leading to the formation of smaller spherulites. Incorporation of natural fibers, such as miscanthus fibers, into a polyester matrix, such as PHBV, was undertaken to enhance the mechanical properties. The inclusion of fiber was utilized to regulate the crystallinity of the composite material. (Smith et al., 2020)

Approaches to sustainable fiber production

In the following, the approaches used in this study to produce sustainable fibers – Wet spinning and spraying, are described.

Wet spinning

The wet spinning process is a fiber synthesis technique that involves the utilization of a polymer solution, a spinneret, and a coagulation bath as shown in Figure 1. In the course of the fabrication procedure, the polymer solution is expelled using a syringe pump through the spinneret and subsequently introduced into a coagulation bath. The formation of

polymer fibers occurs in the coagulation bath as the solvent is eliminated, either through chemical reaction or diffusion (Li et al., 2015). Following the process of formation, the residual fiber material is gathered and subjected to a drying procedure. The act of drawing or subjecting fibers to tension can take place at several stages in the spinning process. It can occur immediately after the spinneret, during the drying phase, or at a later point along the spinning line. The purpose of this drawing process is to elongate the fiber, enhance molecular alignment, and consequently, improve its stiffness and strength (Li et al., 2015; UM, 2004; Lee et al., 2007). According to the study conducted by Qiu et al. (2009), in wet spinning manufacturing methods, the utilization of several drawings or baths is employed with the purpose of enhancing molecular alignment and orientation.

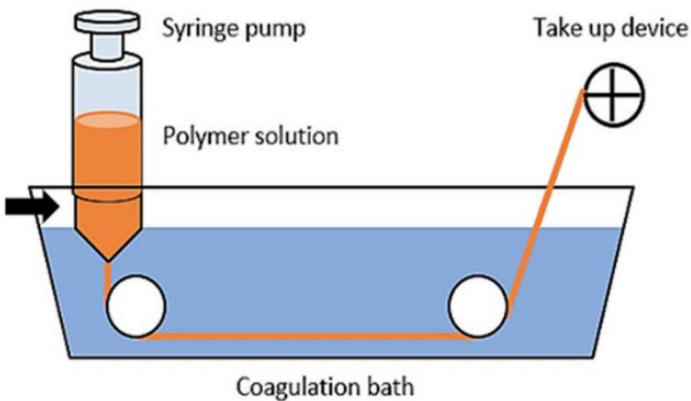


Figure 5. Illustration of wet spinning process (DeFrates et al., 2018)

One specific method is Dry-jet wet spinning, which can be considered as a variation of the wet spinning technique that is shown in Figure 6. It is a chemical fiber spinning method which combines the characteristics of dry spinning and wet spinning. This is a new spinning method developed in the 1960s (Plaza et al., 2011). In the dry-jet wet spinning process, the polymer solution undergoes extrusion through an air gap prior to entering the coagulation bath, as opposed to being immediately introduced into the bath. Research has demonstrated that the employment of dry-jet wet spinning technique leads to enhanced molecular alignment in comparison to the conventional wet spinning method (Lee et al., 2007).

Fiber qualities, including diameter, orientation, and morphology, can be altered by manipulating several factors such as the spinneret diameter, concentration of the polymer solution, and flow rate (Arafat et al., 2015), (UM, 2004), (Li et al., 2015), (Qiu et al., 2009). In contrast to electrospinning, the fibers in this method are not subjected to elevated voltage levels that could potentially cause denaturation of natural polymers, including proteins. Moreover, the act of pulling fibers subsequent to their production has the potential to increase material characteristics by virtue of promoting greater molecular alignment. Nevertheless, it is worth noting that the wet/dry spinning methods often yield fibers that are on the scale of microns, whereas electrospinning is a widely used technique for the production of nanofibers (DeFrates et al., 2018).

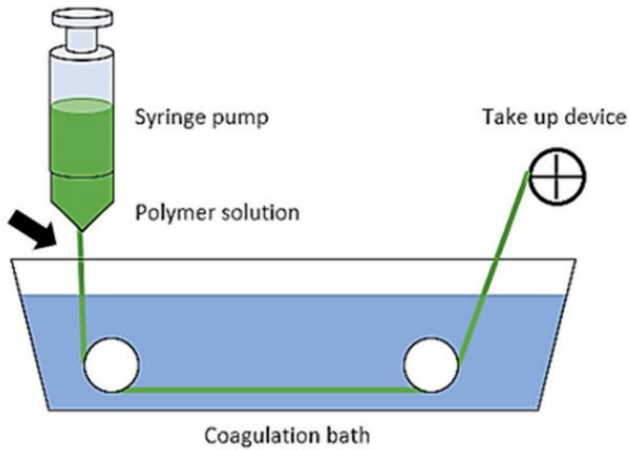


Figure 6. Illustration of dry-jet wet spinning (DeFrates et al., 2018)

Electrospraying

According to Reneker and Chun (1996), electrospraying originated in the early 20th century and began to take shape as a modern concept in the 1960s. One significant application of electrospraying, known as electrospray ionization (ESI), became prominent in the 1980s and revolutionized mass spectrometry (Fenn et al., 1989). Electrospraying has found various applications in the biomedical and pharmaceutical fields, as well as in materials science and nanotechnology. Ongoing research continues to improve the precision, scalability, and versatility of electrospraying, making it relevant in diverse industries (Loscertales et al., 2002).

Electrospraying, also known as electrohydrodynamic spraying, involves the atomization of liquids using electrical forces (Jaworek & Sobczyk,

2008). It offers several benefits over mechanical atomizers, such as the ability to produce droplets with a monodisperse size distribution and the effective manipulation of droplet movement through an electric field (Jaworek & Sobczyk, 2008).

In the context of textiles, electrospraying has been used for coating applications, creating textiles with unique properties such as water repellency and stain resistance (Jaworek & Sobczyk, 2008). It has also been instrumental in the production of smart textiles, which integrate electronics and sensors into fabric (Jaworek & Sobczyk, 2008). Additionally, electrospraying allows for the controlled assembly of nanofibers, resulting in textiles with enhanced breathability, filtration, and barrier properties (Jaworek & Sobczyk, 2008). In the realm of textile finishing, electrospraying offers precise and efficient application of finishes. Researchers have explored electrosprayed finishes for imparting properties such as UV protection, antimicrobial effects, and phase-change materials (PCMs) for thermal regulation. Electrosprayed PCMs, in particular, enable textiles to adapt to temperature changes, offering comfort and energy savings in clothing and bedding applications (Wang et al., 2017).

However, while electrospray offers several advantages in fabric coating and functionalization, it also poses certain challenges. Some disadvantages of electrospray in the context of textiles are the limited

scalability (electrospray is generally more suitable for small-scale applications rather than large-scale production in the textile industry); sensitivity to fabric properties (the effectiveness of electrospray can be influenced by the properties of the textile substrate); potential fabric damage (the high voltage required for electrospray can pose a risk of damaging delicate or sensitive textile materials); compatibility with solvents (electrospray may have limitations in terms of solvent compatibility); and process complexity and equipment cost (implementing electrospray technology for textile applications may require specialized equipment and expertise, increasing the complexity and cost of the production process). During this investigation, the decision was made to examine the phenomenon of spraying of biopolymers for textile applications and to assess it.

The process of spraying with compressed air in textiles includes the atomization of a liquid into small droplets, which are then propelled onto the fabric surface by means of pressurized air. This technique provides several benefits, including consistent and conform coverage, effective penetration, and the capability to create intricate designs and patterns.

There are various process parameters/ conditions that influence produced fiber diameter and nonwoven mat properties. The literature highlights several crucial factors to consider when monitoring spraying methods, including atomization air pressure, concentration of the polymer solution, the solvent used, the substrate on which the solution is sprayed, the number of spray passes, nozzle size, the flow rate of the polymer solution, the temperature of the substrate, the distance between the spray nozzle

and the substrate, and the speed of the moving nozzle during spraying along with the air pressure which transports the sprayed droplets to the substrate. In the case of ultrasonic spraying, the frequency and power settings also play a significant role (Bose et al., 2013), (Trabucco et al., 2021).

Ortelli et al. (2020), in their study on the spray process, focused on three key process parameters: pressure, web speed, and the number of working nozzles. They found that particle number concentration is primarily influenced by the pressure at the spraying nozzle, with a decrease in particle size observed as the pressure increases. Additionally, an increase in particle size was noted with an increasing number of working spray nozzles, possibly due to coalescence phenomena induced by multi-nozzle spraying (Ortelli et al., 2020).

The size of spray droplets is a critical factor that affects coating quality and is influenced by the spray rate and pressure. Generally, droplet size increases with higher spray rates but decreases with increasing spray pressure. It is important to optimize the spray rate to achieve the desired droplet size and prevent sticking, and clogging. The choice of application method and equipment also significantly impacts coating quality (Trabucco et al., 2021).

Sara et al. (2021) concluded that increasing spray pressure from 1 to 1.5 bars enhances deposition efficiency, while an increase in the number of sprays reduces deposition efficiency, indicating that the multiple spray

system is less efficient than the single spray method (Trabucco et al., 2021).

Overall, these findings emphasize the importance of considering and optimizing various process parameters to achieve desired fiber and nonwoven properties, coating quality, and deposition efficiency.

Chapter 3. Results and discussion

In this section, results obtained from the work performed at CITEVE will be presented and discussed.

Results for spraying of polymeric solutions

Observing the images below is possible to see the fiber surface morphology of PVA and PHB sprayed fibers, with different concentrations.

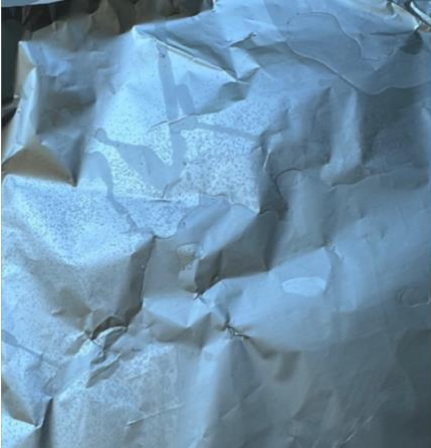


Figure 7a. 5 % w/w PVA sprayed on a collector

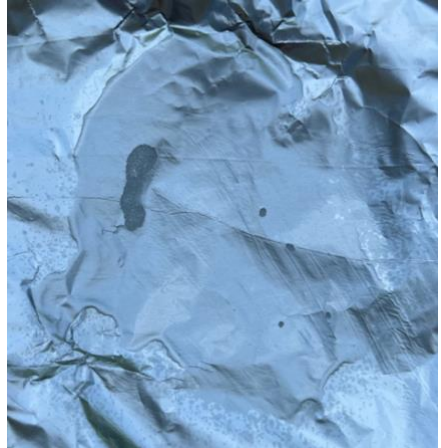


Figure 7b. 2 % w/w PVA sprayed on a collector

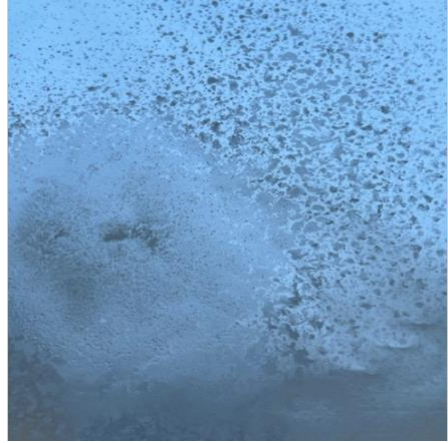


Figure 8a. 10 % w/w PVA sprayed on a collector Figure 8b. 10% w/w PHB dissolved in Cyrene sprayed on collector

No further results are obtained for spraying of polymeric solutions as no film/fiber was produced. Further studies should be conducted on a different equipment to improve the results, testing different solutions with biobased polymers.

Results for dry-jet wet spun chitosan fibers

Visual representation of chitosan fibers

The inability to achieve prolonged fiber strains, as demonstrated in the study conducted by Nechyporchuk et al. (2020) and the experiment conducted by Huang et al. (2021), might be attributed to the absence of rotating spools or take-up rolls. Nevertheless, the visual representation of

the fiber shown in figure 9 has an obvious resemblance to them, with the only difference being its absence of length.

Figure 9 shows the dry-jet wet spun chitosan fibers.



Figure 9. Image of 2 % w/w chitosan fibers

Mechanical properties of the chitosan fibers

An analysis of the mechanical properties of chitosan dry-jet wet -spun fibers was conducted. The results provide valuable insights into the performance of these fibers. The linear mass, represented in decitex (dtex), indicates the weight of the material per unit length. An average

linear mass of 27.0 dtex means that a 1,000-meter-long piece of this material weighs 27 grams. The tenacity, measured in centinewtons (cN) per decitex (cN/dtex), assesses the material's strength relative to its weight. An average tenacity of 1.64 cN/dtex means that a material with a linear mass of 1 dtex would require a force of 1.64 cN to break it, demonstrating its strength. Elongation, expressed as a percentage, reveals the material's ability to elongate before breaking. With an average stretching of 2.79%, it means that the material can stretch approximately 2.79% longer than its original length before breaking. The breaking force, recorded in centinewtons (cN), denotes the maximum force the material can withstand prior to rupture. An average strength of 27.97 cN signifies that, on average, the material can bear a force of 27.97 cN before breaking, emphasizing its robustness. Moreover, the standard deviation measures the variation in these properties, aiding in our understanding of data consistency. The coefficient of variation, expressed as a percentage, provides insights into the relative variability of the measurements. Furthermore, the minimum and maximum values showcase the range of recorded data. Lastly, the confidence interval gives us an estimate of the potential range within which the true population parameters may reside, offering valuable information regarding measurement reliability. These results not only characterize the mechanical properties of chitosan fibers but also provide essential data for evaluating their quality and performance specifically in textile applications.

Chitosan fibers possess a great fineness and strength in comparison with results obtained from different literature such as work done by Bao et al. (2019) and study conducted by Kuznik et al. (2022). For elongation of the chitosan fibers our study shows improvements in comparison with chitosan fibers obtained by Zhu et al. (2019). However, elongation and tenacity show 5 times lower values when compared to Bao et al. (2019) and Kuznik et al. (2022). As for breaking force, it is significantly better than Bao et al. (2019) chitosan fibers. Although, chitosan fibers wet-spun by Kuznik et al. (2022) have twice better results.

Table 1. Mechanical properties of dry-jet wet spun chitosan

	Linear Mass (dtex)	Tenacity (cN/dtex)	Elongation (%)	Breaking force (cN)
Average value	27.0	1.64	2.79	27.97
Standard deviation	13.7	1.37	0.29	0.48
Coefficient of variation (%)	50.7	83.5	10.2	10.2

Minimum	4.92	0.56	2.34	24.62
Maximum	50.1	5.70	3.58	28.11
Confidence interval	3.89	0.39	0.08	0.14

Examination of fiber surface morphology for dry-jet wet spun produced chitosan fiber

Images below show SEM analysis of the chitosan fibers.

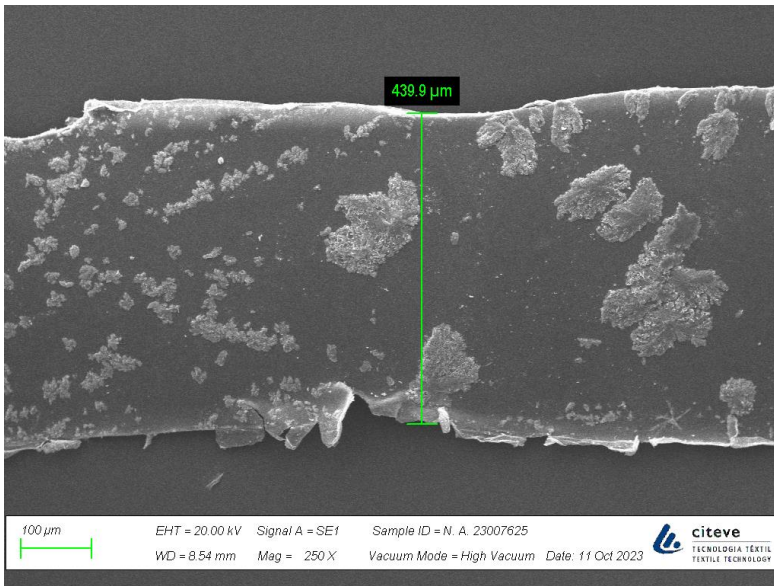


Figure 10. SEM image of chitosan fiber without the updated washing process step (diameter indicated by a green line)

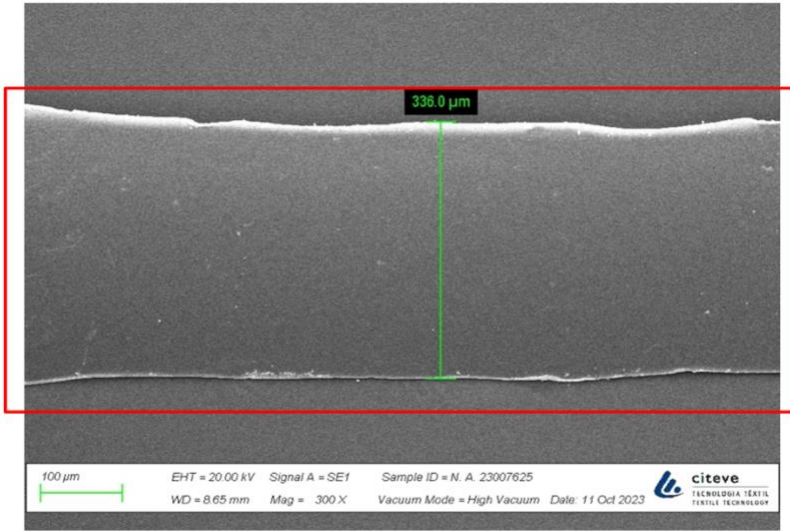


Figure 11. SEM image of chitosan fiber without the updated washing process step (sample boxed with a red line, diameter indicated by a green line)

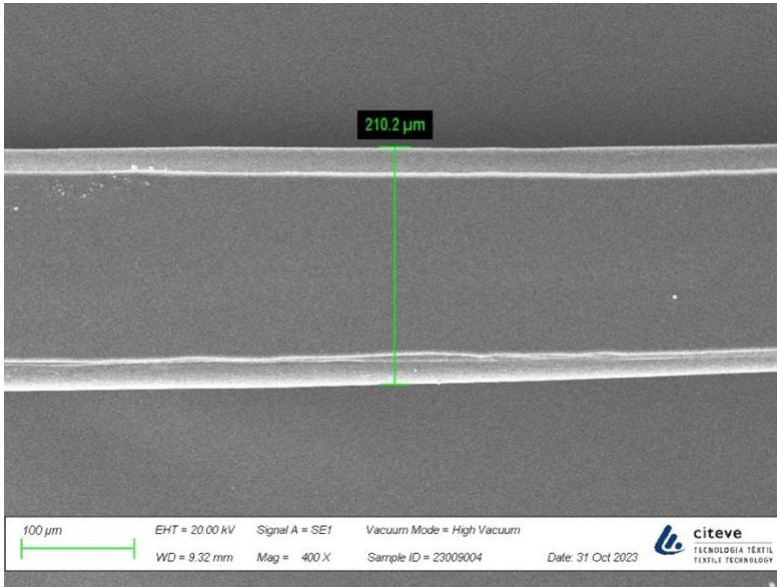


Figure 12. SEM image of chitosan fiber after the updated washing process (diameter indicated by a green line)

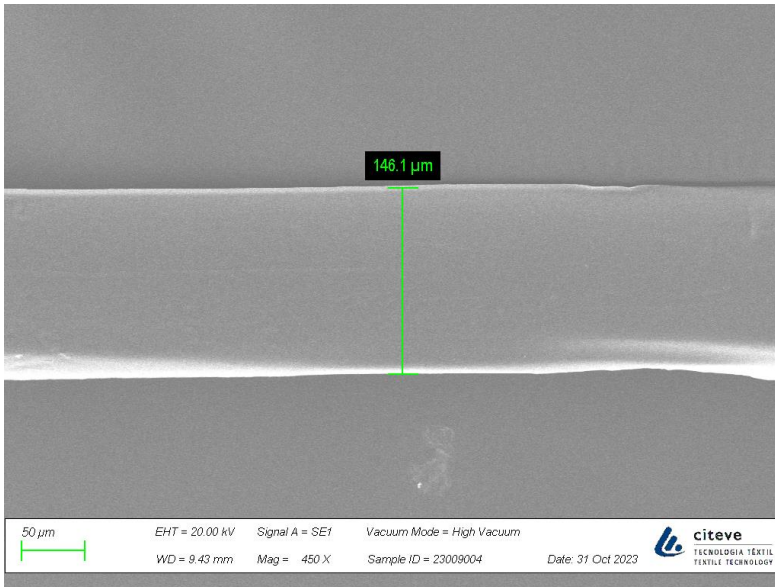


Figure 13. SEM image of chitosan fiber after the updated washing process (diameter indicated by a green line)

Elemental composition of samples

Chitosan fiber without the updated washing process

Figure 14 and Table 2 show EDS results.

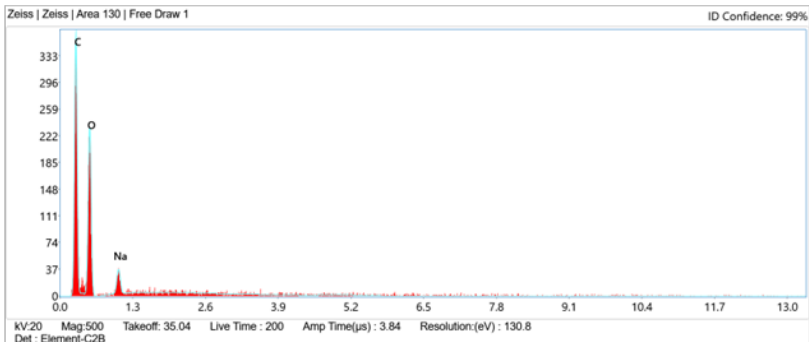


Figure 14. EDS result of dry-jet wet spun chitosan fibers

Table 2. EDS results of dry-jet wet spun chitosan fibers

Element	Weight %	MDL	Atomic %	Error %	Net Intensity	R	A	F
C K	61.9	32.48	68.7	11.7	10.3	0.9372	0.1691	1.0000
O K	36.4	38.16	30.4	13.1	7.4	0.9450	0.0812	1.0000
Na K	1.6	13.38	0.9	18.1	1.2	0.9537	0.2838	1.0012

Chitosan fiber after the updated washing process

EDS results are shown in Figure 15 and Table 3.

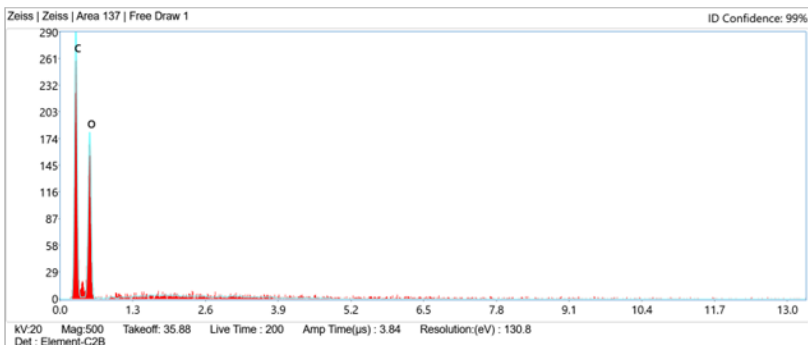


Figure 15. EDS result of wet-spun chitosan fibers after updated washing process

Table 3. EDS results of dry-jet wet spun chitosan fibers after updated washing process

Element	Weight %	MDL	Atomic %	Error %	Net Intensity	R	A	F
C K	63.3	0.72	69.7	11.7	8.7	0.9378	0.1822	1.0000
O K	36.7	0.66	30.3	13.5	5.7	0.9456	0.0817	1.0000

Textile structure based on dry-jet wet spun chitosan fibers.

The textile structure containing the chitosan fibers, aiming for medical applications is shown in figure below.

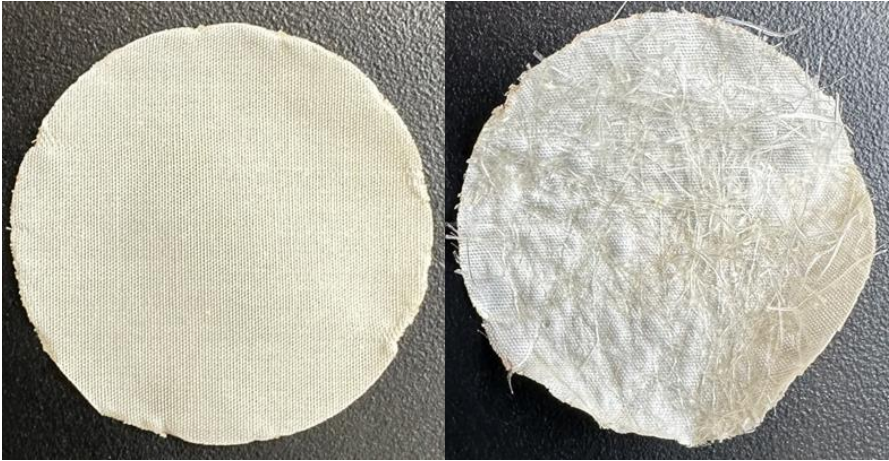


Figure 16. Textile structure containing the chitosan fibers, aiming for medical applications (from left to right – 100% cotton woven fabric (left) and 100% cotton woven fabric coated with dry-jet wet spun chitosan fibers (right))

Antibacterial activity for the coated fabric was studied and figures below show the results from this analysis.

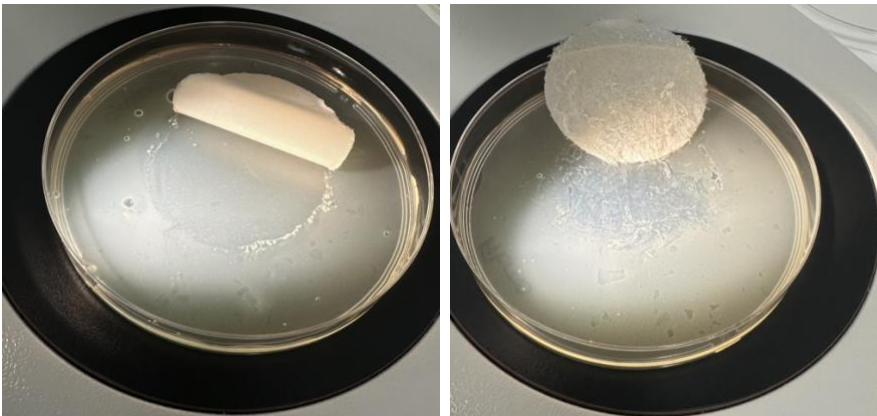


Figure 17. From left to right: 100% cotton woven fabric in PCA and coated fabric with chitosan fibers in PCA

Discussion for spraying of polymeric solutions

Analyzing the figures in the Results section, it is possible to see that there were not sprayed fibers. The behavior of the solution coming out of the nozzle was similar to water coming out of a tap and it is not similar to a spray. Most of the time, some drops coming out were showing some type of clogging. The attempt to address the clogging and viscosity issues in the PVA spraying method included the preparation of solutions with different concentrations. This strategy aimed to determine whether adjusting the solution's concentration could alleviate these challenges and improve the overall quality of the spraying process. Additionally, the application of another biopolymer, namely PHB, dissolved in dihydrolevoglucosenone (commonly known as Cyrene), a recognized environmentally friendly solvent, was employed instead of PVA for the purpose of spraying. In this case, 10 % w/w PHB in Cyrene showed the same result as PVA spraying.

One of the main obstacles was proved to be clogging mitigation. By varying the concentration of the PVA solution, it was anticipated that the risk of clogging the irrigation nozzle might be reduced. Solutions with

lower viscosity, resulting from decreased PVA concentration, were expected to flow more smoothly through the nozzle, minimizing clogging issues. This approach was adopted to find an optimal solution concentration that would balance fiber quality and process reliability.

The viscosity of the solution plays a pivotal role in the sprayability of the material. A solution that is too viscous can lead to clogging and wrong spray patterns, while a solution with low viscosity may compromise the integrity and structure of the sprayed fibers. By preparing solutions with different concentrations, the goal was to identify an equilibrium point where viscosity was manageable, and fiber quality was maintained.

However, the inability to modify any parameters due to having simple spraying equipment with only nozzle and pump which rate couldn't be changed was a significant constraint in identifying the underlying issue. Based on current observations, it is evident that complete dissolution is necessary, and the viscosity must be appropriately adjusted.

In conclusion, the preparation of PVA solutions with different concentrations aimed to address the challenges of nozzle clogging and solution viscosity. By systematically testing and evaluating these solutions, a better understanding of the interplay between concentration and successful fiber production was gained. This knowledge can inform future attempts to optimize the PVA spraying method. Furthermore, the implementation of advanced equipment that allows for precise control of pressure and flow rate will result in enhanced efficiency in material utilization and production processes.

Discussion for dry-jet wet spun chitosan fibers

The fibers produced have a flatter and irregular morphology, presenting a certain rigidity, being brittle (Figure 9). The mechanical properties of chitosan fibers are of paramount importance, as they play a pivotal role in determining the suitability of these fibers for various applications. The data obtained in this study provide valuable insights into the performance of chitosan fibers, particularly with potential applications in the textile industry.

The study conducted by Bao (2019) was selected for discussion due to its use of wet spinning techniques for chitosan in the same coagulation bath. Chitosan fibers possess a mass per unit length, as seen by their average linear mass, of roughly 27.0 dtex. In the study conducted by Bao (2019), the researchers obtained a mean value of 9.78 ± 0.64 dtex. Based on the findings of this thesis, it can be inferred that the wet-spun fibers prepared in this work exhibit superior fineness. This particular attribute holds considerable importance, particularly within the realm of textile applications, as it exerts impact over variables such as fabric weight and texture. Additional optimization may be required in order to fit this particular characteristic with the specific requirements of textiles.

The average tenacity of 1.64 cN/dtex implies that chitosan fibers possess a moderate to good tensile strength for wet-spun chitosan fiber. In comparison with other literature references like (Zhu et al., 2019), our

fiber show improvements in tenacity. On the contrary, there are wet-spun fiber that showed 5 times greater tenacity, such in the study done by (Bao et al., 2019) and in the experiment by Kuznik et al. (2022) were fibers average tenacity is around 4.51 cN/dtex. It is worth noting that tenacity is a critical parameter for textiles, as it determines the ability of the fibers to withstand stress and strain. In the context of textile production, achieving higher tenacity may be beneficial to enhance durability.

The average stretching capability of 2.79% is a valuable parameter for applications where flexibility and elasticity are required. The value presented in this study, when compared to the wet-spun chitosan fibers investigated by Bao et al. (2019), suggests the potential for further enhancement. Chitosan fibers show a promising ability to elongate, but further research might explore approaches to enhance this characteristic.

The average strength of 27.97 cN indicates that the chitosan fibers possess a reasonable resistance to rupture. According to the study conducted by Bao et al. (2019), the strength of their sample was measured to be 5.13 ± 0.35 cN. In contrast, the average strength of the chitosan wet-spun material in this thesis was found to be 27.97 cN, with a standard deviation of 0.48. This characteristic renders it comparatively robust given its inherent qualities. In textiles, it is crucial for withstanding mechanical stresses during usage.

The data's standard deviation and coefficient of variation suggest that there is significant variability in the mechanical properties of chitosan fibers. This variability may arise from factors such as processing conditions, the source of chitosan, or the presence of impurities. Further research and optimization of production methods can help reduce this variability, enhancing the consistency of the fibers.

When considering the potential application of chitosan fibers in the textile industry, the results indicate that these fibers could be used in blends with other natural or synthetic fibers to achieve specific properties. Blending chitosan with cotton, for example, might yield textiles with enhanced strength and moisture-wicking capabilities, desirable for sportswear.

The detection of sodium (Na) in the EDS analysis of the chitosan fibers is likely a result of the coagulation procedure involving the use of a 1:1 mixture of 10% solution of NaOH and EtOH solution. The coagulation of chitosan fibers in a sodium hydroxide solution can lead to the incorporation of sodium ions from the coagulation bath into the fiber structure. This phenomenon is frequently observed when fibers or materials undergo processing in solutions that contain certain ions. This process can introduce sodium into the chitosan fibers, which is consistent with the presence of sodium in the EDS data.

To minimize the presence of sodium in the chitosan fibers, thorough washing and rinsing steps with deionized water after coagulation may help remove any surface-bound or loosely attached sodium ions. However, it has been observed that a single rinsing step during the washing process in a beaker filled with distilled water is insufficient to effectively remove ions or particles that may adhere to the fibers during coagulation.

Following the detection of sodium (Na) in the EDS analysis, a rigorous cleansing procedure was undertaken. The fibers were subjected to a thorough washing process involving three sequential rinses with distilled water. Throughout this cleansing regimen, gentle stirring was employed to ensure the efficient removal of any residual sodium content. Subsequent to this treatment, the analytical results revealed the complete elimination of sodium within the fiber samples.

Furthermore, the SEM imagery post-washing exhibited marked improvements, characterized by a heightened degree of cleanliness and homogeneity. The irregular and non-linear edges observed in the SEM images depicted in Figures 6 and 7 can be attributed to the effects of the drying process.

The presented data reflects the elemental composition of the sample as determined by EDS. This analysis identified two significant elements within the chitosan fibers: carbon (C) and oxygen (O). The weight percentages represent the portion of each element within the sample.

For the carbon element, it comprises approximately 63.3% of the sample, with an associated atomic percentage of 69.7%. This indicates a slight discrepancy between the weight and atomic percentages, implying a level of error or irregularity within the measured sample. The error percentages associated with both elements, carbon, and oxygen, are within an expected range, suggesting a degree of measurement accuracy.

The net intensity of the elemental signals for carbon and oxygen shows good reliability and a significant level of confidence in the obtained data. These signals, with values close to 1.0000, denote strong and consistent detection of both elements in the sample, adding credibility to the measurements.

The abundance of carbon in the chitosan fibers aligns with the known composition of chitosan, which is primarily a carbohydrate-based polymer primarily composed of carbon, hydrogen, and oxygen. The results indicate a high carbon content, a characteristic of organic polymers, in this chitosan-based fiber. The relatively lower oxygen content compared to carbon also fits the expected profile of chitosan, where the primary composition is carbon and hydrogen, with fewer oxygen atoms.

Overall, the EDS data provides valuable information regarding the elemental makeup of the chitosan fibers, which is consistent with expectations for this organic material.

The textile structure developed in this investigation involved the application of dry-jet wet spun fibers and chitosan solution as an adhesive. Notably, this textile structure exhibited antibacterial properties, as depicted in Figure 17. It can be observed that the control fabric, composed 100% cotton, has no impact on bacterial growth. This is evident from the presence of a non-translucent region beneath the fabric, which serves as evidence of bacterial proliferation. When comparing coated fabric with uncoated fabric, it becomes evident that the region in direct touch with the fibers is clearer and more transparent, indicating the absence of bacterial growth. It is imperative to acknowledge that the testing was conducted on a single sample. In further investigations, it is recommended to conduct a greater number of tests employing multiple samples to corroborate the antibacterial efficacy of the textile structures.

Further research and development are needed to optimize properties in general for specific uses in the textile industry.

Chapter 4. Experimental

In this section the experimental procedures are described.

Preparation of PVA solutions for spraying

5% w/w PVA Solution

In the preparation of the 5% w/w PVA solution, 2.5 grams of PVA (equivalent to 56.8 mmol) were introduced into a mixture of 0.5 mL of dimethylformamide (DMF) and 49.5 mL of distilled water. The solution was subjected to magnetic stirring at a temperature of 60°C for a duration of 30 minutes.

2% w/w PVA Solution

A 2% w/w PVA solution was prepared 4 grams of PVA (equivalent to 9.1 mmol) that were combined with 20 mL of distilled water. The solution underwent magnetic stirring for 30 minutes.

10% w/w PVA Solution

For the 10% w/w PVA solution, a quantity of 10 grams of PVA (equivalent to 0.2272 mol) was blended with 90 mL of distilled water. Magnetic stirring was conducted for an extended period of 2 hours at a temperature of 80°C.

10% w/w PHB solution

A 10% w/w PHB solution was prepared from the partner institution from the Waste2BioComp EU project. The solution was dissolved in Cyrene.

Dry-jet Wet Spinning Process

Preparation of 2% w/w Chitosan Solution

A 2% w/w chitosan solution was prepared by dissolving 10 g of chitosan (equivalent to 61.1 mmol) in 200 mL of distilled water. To aid in dissolution, 3 mL of acetic acid was added to the mixture, and stirring was continued until complete dissolution was achieved. Distilled water was then added to bring the total solution volume to 500 g.

Preparation of coagulation bath

The dry-jet wet spinning process involved the use of 2 coagulation baths 1 M NaOH, and another 1:1 mixture of 10% w/w solution of NaOH and EtOH. Each coagulation bath had a volume of 500 mL, and the pH of the bath was measured at approximately 13.43 for 1 M NaOH and 13.37 for mixture of 10 % solution of NaOH and EtOH.

Both coagulation baths produced excellent results. Nevertheless, the use of a 10% NaOH solution in combination with ethanol demonstrated a higher degree of environmental sustainability when compared with the 1 M NaOH solution. The use of a bath solution consisting of a 10% concentration of NaOH, and ethanol not only yielded favorable outcomes

but also matched to sustainable principles, hence facilitating the generation of additional fibers in an environmentally conscious manner.

The chitosan solution was pumped into the coagulation bath at an optimal pumping rate of 36 mL/min with a volume set to 35 mL and diameter of 30 mm.

The process involved pumping the chitosan solution into a coagulation bath while gently stirring for improved coagulation.

Washing

The initial washing process consisted of singular rinsing with distilled water without any stirring for about 5 minutes. However, after analyzing the fibers by SEM the washing step was improved to obtain better fibers. This updated washing process involved three consecutive rinses with distilled water, with each rinse using fresh distilled water. To prevent damage to the delicate fibers, a beaker was used for the rinsing process. Gentle agitation was applied during each rinse, taking care not to subject the fibers to excessive mechanical stress. Each rinse cycle lasted approximately 2 minutes.

Drying

The drying process was carried out at room temperature, where the fibers were stretched within a petri plate and left to air-dry for about 3-4 hours.

This method allowed for a controlled drying environment in ambient conditions, contributing to the overall efficiency of the process.

Chapter 5. Materials and methods

The research unfolds through an experiential journey, combining literature exploration and laboratory experimentation within the Research and Development departments of the biotechnology and chemistry divisions at CITEVE.

Materials

In the course of conducting the experiments, several essential materials were employed to facilitate the research and obtain meaningful results.

For experiment with spraying method, the key materials included: PVA, which was obtained from Sigma-Aldrich in the Netherlands. This specific PVA variant had a hydrolysis level between 87-90% and featured a molecular weight within the range of 30,000 to 70,000. Distilled water served as the primary solvent for various solutions in the experimental process. Dimethylformamide (DMF), a high-purity reagent grade solvent with a molecular weight of 73.09, was used for specific stages of the experiment. Additionally, a solution of PHB with Cyrene was provided by a partner institution from the Waste2BioComp EU project.

For experiment of dry-jet wet spinning method, a distinct set of materials was selected to fulfill the research objectives. This included chitosan (Chitoclear cg 800), characterized by its viscosity within the range of 600-1200 mPa·s and a calculated molecular weight of 300–340 KDa. The quality of chitosan was crucial for the reliability of the outcomes. Acetic Acid (Glacial), manufactured by Ensure, and featuring a purity level of 100%. It served as a critical component of the experiment. Sodium Hydroxide (White Pellets), supplied by Fisher BioReagents, and Ethanol Absolute Anhydrous from Carlo Erba Reagents were integral components in the coagulation process, contributing to the overall success of the research. Once again, distilled water was utilized as a solvent and played a role in the coagulation bath, ensuring the reliability and accuracy of the research outcomes. These carefully selected materials were pivotal in achieving the research goals and obtaining credible results.

For the coated fabric with dry-jet wet spun fibers it was used: a 100% cotton woven fabric; chitosan solution produced for the dry-jet wet spinning as a type of “glue” to fix the chitosan fibers to the fabric; and, finally, dry-jet wet spun chitosan fibers.

Methods

Spraying and dry-jet wet spinning methods are explained below, as well as the production of the textile structure.

Spraying

The spraying experiment was conducted using custom-made spraying equipment provided by CITEVE. This equipment comprised a pump, with a maximum flow rate of 1.5 - 2 L/min, and nozzle typically used for irrigation systems.

The setup involved spraying a solution from the nozzle at a distance of 15 cm to a collector, which consisted of a simple aluminum foil surface. The spraying time was precisely controlled and set at 10-15 seconds for each experiment. This arrangement allowed for the controlled application of the solution onto the collector.

This spraying experiment aimed to achieve specific objectives, which were outlined in the research design. The collected data and observations from this experiment were crucial for further analysis and drawing conclusions regarding the properties of the sprayed material.

The specific parameters, such as the composition of the solution, spraying duration, and any additional controls, were defined according to the experimental requirements.

The spraying experiment was carried out under controlled conditions to ensure the accuracy and reproducibility of the results.

Figure 18 illustrates the setup for spraying of polymeric solutions.

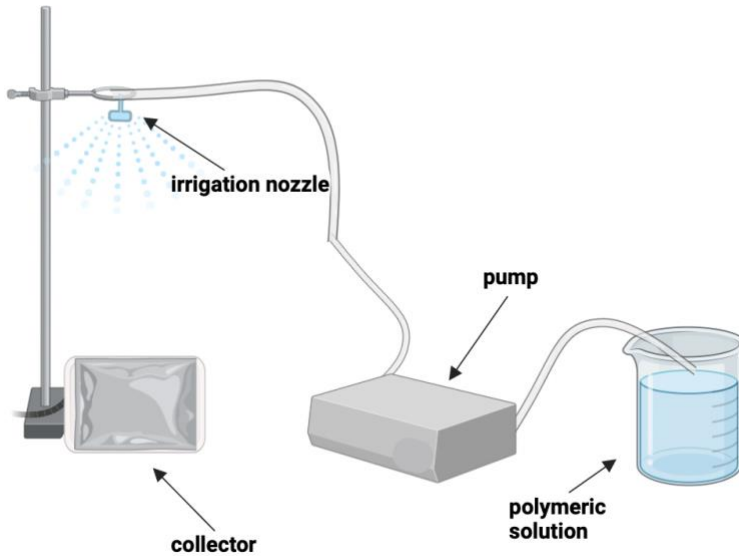


Figure 18. Illustration of setup for spraying of polymeric solutions

The present experiment serves as a first investigation into the use of polymeric solution spraying. The intention is to utilize the newly depicted spraying apparatus for the production of polymeric fibers using spraying approach. It was chosen AutoJet[®] E1850+ Spray System from Spraying Systems Co (Figure 19).



Figure 19. AutoJet® E1850+ Spray System (AutoJet® Model E1850+ Spray Controller | Spraying Systems Europe, n.d.)

The AutoJet® E1850+ Spray System is designed to be a perfect fit for nearly every spray application. The system optimizes the performance of your automatic spray nozzles for an efficient use of resources and a high-quality end result. Figure below shows some details of the spraying equipment.

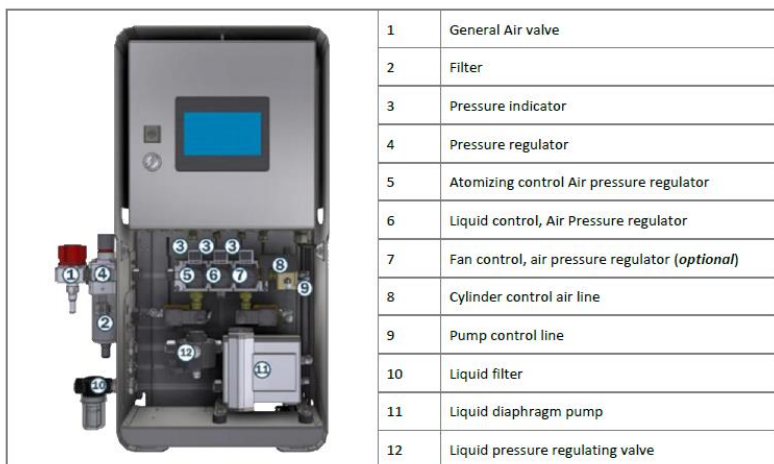


Figure 20. Details of spraying equipment (obtained from CITEVE)

Regarding nozzles it will be used three types: ultrasonic; hydraulic and pneumatic.

Dry-jet wet spinning

In the experimental setup for fiber production, a specially designed dry-jet wet -spinning apparatus was employed, which featured the use of a syringe pump. This apparatus was crucial for the successful creation of the fibers. The spinning process was further facilitated through the utilization of a Model: NE-1000 Multi-Phaser™ syringe pump, which belonged to the NE-1000 Series of Programmable Syringe Pumps. This syringe pump operated on Firmware Version: V3.923 and offered a wide range of pumping rates, starting from 0.73 $\mu\text{L}/\text{h}$ when using a 1 mL

syringe, and scaling up to 2120 mL/h when equipped with a 60 mL syringe. The equipment was sourced from New Era Pump Systems Inc., a reputable company located in Farmingdale, NY, USA.

To ensure the accuracy and precision of the dry-jet wet spinning method, additionally to a syringe pump, a magnetic stirrer was incorporated into the experimental setup.

The combination of the wet spinning apparatus and the Model: NE-1000 Multi-Phaser™ syringe pump provided a controlled and effective means of generating the fibers, allowing for reliable and reproducible results in the research. The use of this specialized equipment was fundamental to the success of the experimental procedure.

The syringe needs to be immersed or have distance from needle to coagulation bath solution maximum 2-3 cm in order to form homogenous fibers. The setup used is shown in Figure 21.

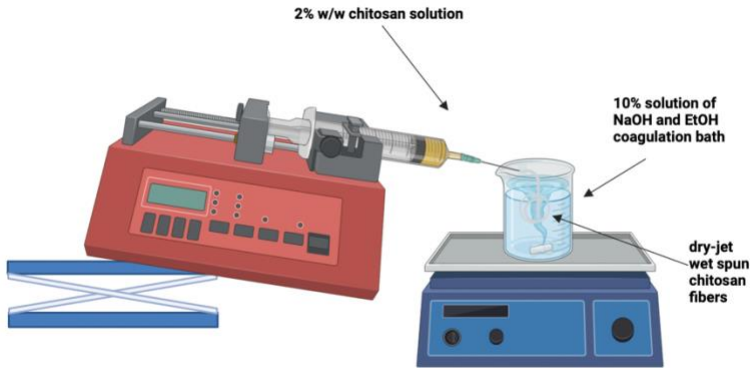


Figure 21. Illustration of the setup for the chitosan fiber's dry-jet wet spinning

Regarding physical, chemical, and mechanical analysis, approaches below were applied:

- Fiber surface morphology – microscopic observations of fibers were carried out in a scanning electronic microscope, using model Evo 10 from Zeiss;
- Chemical constitution – using SmartEDX EDS Analysis System;
- Linear density – according to EN ISO 1973:2021 standard, using 50 samples with 20 mm of length. Applied elongation speed was 20 mm/min, with pretension of 1 cN/tex;
- Mechanical characterization - EN 5079:2020 standard was followed. Samples were conditioned at $20\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ and $65\% \pm 4\%$ humidity for 24 h. Specimens were 10 mm long; tensile speed

was 20 mm/min and a pretension of 1 cN/tex was applied. 50 replicas were tested.

Samples were conditioned at $20\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ and $65\% \pm 4\%$ humidity for 24 h. These conditions were also kept during testing. All tests were done by certified laboratories from CITEVE.

Textile structure

The manual fabrication process was employed for the production of the chitosan fiber-coated textile structure. Chitosan solution was employed in the dry-jet wet spinning process as an adhesive agent for attaching chitosan dry-jet wet spun fibers onto a substrate made up of 100% cotton woven fabric. Following the fixation of the fibers on the fabric surface, the samples were subjected to a drying process in an oven set at a temperature of $50\text{ }^{\circ}\text{C}$ for a duration of approximately 30 minutes.

A preliminary test, namely Plate Count Agar (PCA), was conducted in order to assess the antibacterial activity against *Escherichia coli*. An internal technique was implemented, utilizing ISO 20645:2004 as the basis. A single replica was subjected to testing.

Chapter 6. Conclusion

In conclusion, this research journey was marked by exploration, innovation, and the relentless pursuit of sustainable fiber production. Objectives were twofold: to develop fibers using bio-based polymers and proteins, and to explore novel manufacturing techniques while ensuring that the resulting fibers hold exceptional promise in the context of the textile industry sector. As to reflect on findings, it should be considered the diverse paths that led to both success and challenges.

The investigation into protein-based fibers, epitomized by chitosan fibers, underscores their potential as a cornerstone of sustainable material development. Beyond the synthesis process, it was diligently probed the mechanical properties, revealing the strength, flexibility, and versatility of these fibers for a wide array of applications in the world of apparel.

Simultaneously, the journey into PVA fibers revealed the complexities inherent in the quest for sustainability. Despite the best efforts, limitations in the pump and nozzle mechanisms led to an unsuccessful attempt. In response, different concentrations of solutions were explored to understand whether viscosity or clogging was a contributing factor.

The wet spinning method proved to be effective in producing chitosan fibers, while washing with distilled water resulted in fibers that are free

from contaminants such as Na. However, it was observed that washing may lead to a slight reduction in fiber diameter, potentially due to the removal of impurities.

The SEM images have provided valuable visual data, showing the morphology and structure of chitosan fibers. These images will contribute to a deeper understanding of the fiber's physical characteristics.

While challenges and limitations have been encountered, such as the issue of fiber diameter reduction and the need for improved mechanical properties, these results point to opportunities for further research and development. Chitosan fibers, when optimized, could find applications in fields like the textile industry or tissue engineering, where sustainable materials with tailored mechanical properties are in demand. Furthermore, the conducted antimicrobial tests provide potential for the utilization of these chitosan fibers in the field of biomedical textiles. Although the subject was evaluated previously, it is recommended that further tests be done in order to enhance confidence in its applicability.

The findings from this research contribute to the larger discourse on sustainable fibers and manufacturing techniques. As the textile industry seeks eco-friendly alternatives, chitosan fibers hold promise, providing a

steppingstone towards a more environmentally conscious and sustainable future.

As to contemplate these diverse outcomes, it is vital to recognize that both successes and challenges are integral components of the research process. The lessons learned from these attempts, even when they did not yield the desired results, contribute to a deeper understanding, and offer valuable insights for future endeavors.

This study project can be conceptualized as a dual effort, covering an investigation into the new field of sustainable fiber production, and serving as a starting point for future advancements. The key goal is to change the textile industry towards a more sustainable and ecologically conscious approach. The ongoing path continues, as does the dedication to enhancing sustainable practices within the textile industry moving forward.

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