UNIVERSITY OF TARTU
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Unsupported Solution Blow Spinning: Dependence on Polymer, Solvent, and Blowing Parameters

Master's Thesis (30 ECTS)

Bioengineering

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Abstract:

Fabrication of unsupported micro/nanofiber structures using Solution Blow Spinning (SBS) is a versatile method for creating fine fibers with potential applications in various fields such as biomedicine, filtration and soft robotics. While many methods exist for investigating non-woven tensile properties, the self-tensioning behavior of fibers post-spinning is less explored. This study addresses this gap by focusing on how internal tensions within the fibers influence their structure. The primary focus is on developing and refining methodologies to optimize fiber formation for applications requiring unsupported, freestanding structures during spinning. This work varied the solution composition, the type of polymer and solvent used, and incorporating additives like ionic liquids to enhance fiber formation properties. A methodology was developed for investigating tensioning of fibers post-spinning. Polyethylene oxide revealed limitations due to inadequate post-tensioning properties, the fibers were not able to endure their own tensioning force and ruptured. Poly(vinylidene fluoride-co-hexafluoropropylene) showed potential yet also faced challenges in maintaining structural integrity under tension. Incorporating 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid into the poly(vinylidene fluoride-co-hexafluoropropylene) solution enhanced post-tensioning and reduced material fractures. This modification led to fibers capable of sustaining higher strains making them suitable for robust structural applications such as biomedical scaffolds. The study establishes a framework for the scalable production of unsupported fiber structures. The findings suggest that with further optimization, SBS could be used to produce different unsupported fiber-based constructs directly on anchors/supports instead of creating the structures after achieving supported fibrous mats.

Keywords:

Solution Blow Spinning, Unsupported Fibers , Polyethylene Oxide, Poly(vinylidene fluoride-co-hexafluoropropylene), Ionic Liquids, Post-tensioning, Biomedical Scaffolds.

CERCS:

T490 Biotechnology

Toevaba õhuketrus: polümeeri, solvendi ja ketrusparameetrite mõju

Kokkuvõte:

Toevaba õhuketrus on mitmekülgne meetod mikro- ja nanofiibritest struktuuride valmistamiseks, millel on potentsiaalsed rakendused näiteks biomeditsiinis, filtermaterjalina ja pehmerobootikas. Kuigi on olemas mitmeid meetodeid lausriide mehaaniliste omaduste määramiseks, on kiudude isepinguldumine pärast ketrust vähe uuritud. Käesolev töö keskendub kiudude ketrusel kogunevate sisepingete ehk isepunguldumise ja struktuuri vaheliste seoste uurimisele. Töös arendatakse välja meetod toevabalt õhukedratavate lausmaterjalide isepinguldumise uurimiseks ketruse käigus. Meetodit rakendatakse seejärel ketruslahuse koostise, sealhulgas kasutatava polümeeri ja lahusti mõju uurimisel. Polüetüleenoksiidist kiud purunesid isepinguldumisel. Polüvinülideenfluoriid-ko-heksafluoropropüleenist struktuur säilus paremini, kuid kaotas kiiresti pingsuse. Uuriti voolise lisandi mõju kiumoodustumisele. Voolise 1-etüül-3-metüülimidasooliumtrifluorometaansulfonaadi lisamine polüvinülideenfluoriid-ko-heksafluoropropüleeni lahusesse suurendas isepingulduse määra ning vältis materjali purunemise ning isepingulduse kao. Voolise lisamine võimaldas kiududel taluda kõrgemaid pingeid, muutes need perspektiivikaks kasutada tugistruktuuride, näiteks biomeditsiiniliste rakumaatriksitena. Uuring pakub välja raamistikku kiuliste struktuuride toevaba ketruse skaleerimiseks. Töö tulemused viitavad, et edasise optimeerimise tulemusena võib õhuketrust kasutada erinevate lausmaterjalist konstruktsioonide paigutamiseks otse tugistruktuuridele ilma vahepealse kiudmatisammuta.

Märksõnad:

õhuketrus, toevaba ketrus, polüetüleenoksiid, polüvinülideenfluoriid-ko-heksafluoropropüleen, voolised, isepinguldumine, biomeditsiinilised rakumaatriksid.

CERCS:

T490 Biotehnoloogia

Table of Contents

INTRODUCTION

Nano- and microfibers have unique qualities such as high surface area-to-volume ratio, high porosity, and mechanical properties that may be adjusted. These qualities make them particularly appealing for a variety of uses in industries like filtration, energy storage, environmental remediation, and biomedicine. In air filtration, nanofibers enhance filter efficiency in capturing particles due to their small diameters and high surface areas (Barhate & Ramakrishna, 2007). In the field of energy storage, nanofiber-based electrodes offer increased surface area, improving energy density and charge rates, making them useful in applications like lithium-ion batteries and supercapacitors (Silva et al., 2024). Nanofibers are also used in environmental remediation for absorbing toxic spills and heavy metals (Khosravifar et al., 2024). In biomedicine, nanofibers are ideal for tissue engineering applications due to their ability to support cell attachment and proliferation, mimicking the extracellular matrix (Zhang et al., 2005). Solution Blow Spinning (SBS) is a technology that stands out among others because it is easy to use, versatile, and adaptable. SBS provides a quick and effective way to produce micro- and nanofibers by dispersing polymer solutions using a high-speed gas jet (Wang et al., 2016). The potential of this approach to address various issues, such as improving efficiency in filtration systems, enhancing the mechanical properties of biomedical scaffolds, and developing advanced materials for energy storage, attracts attention for further research.

The potential of SBS to directly deposit fibers onto a variety of anchors and supports to generate freestanding nano- and microfiber structures is explored in this thesis. Given that the existing uses of SBS are primarily concerned with developing supported fiber mats rather than freestanding structures, this topic is relevant to advancing applications in different fields tissue engineering, soft robotics, and other fields by introducing fabrication methods for unsupported structures. SBS's capacity to create fibers with specific characteristics by varying the parameters of polymer solutions is highly intriguing for a variety of application areas. However, a few unidentified variables might be at play because there has not been abundant systematic research on unsupported structures. These structures may lead to new and innovative applications in tissue engineering, robotics, and other fields. This work focuses on comprehending the process of constructing freestanding structures. It seeks to develop the methodology for creating unsupported structures and to evaluate their physical characteristics, tensile strength, and potential applications. This involves developing new methodologies to investigate self-tensioning on unsupported structures, and other factors related to unsupported spinning. As well as it aims to assess how various polymer solutions and additives—particularly ionic liquids—affect the deposition and physical parameters of the fibers. This includes an analysis of the fibers' post-tensioning effects, which is a phenomenon where internal tensions are retained within the fiber structure after the SBS process has finished. Post-tensioning is critical in freestanding structures as it impacts the fibers more than non-freestanding structures due to lack of full support and this work seeks to enhance our understanding of unsupported structures and facilitate their practical application in various real-life scenarios.

1. LITERATURE REVIEW

1.1. Methods for micro/nano fiber creation

1.1.1. Classification

Various methods are used to fabricate fine nano/micro scale fibers, each having unique mechanics and uses. A fundamental representation of spinning applications is the spinning of polyester to manufacture clothes, a process encountered in daily life. This serves as a primary example of how fibers are utilized in various industries. All of the methods that produce non-wovens are mostly collected together as a mat. However, the actual fiber production aspect between the methods varies. Melt spinning is a commonly used technique that creates continuous fibers by melting a polymer and extruding it through a spinneret, where shear forces are applied to align the polymer chains and facilitate the formation of fibers. This method works only with thermoplastic polymers, which solidify when cooled from melt to provide continuous filament yarns for use in textile applications (Hufenus et al., 2020). Melt blow spinning (MBS) is a variant of melt spinning where thin fiber diameter nonwoven fabrics are produced by extruding molten polymer streams into micro/nano fibers using high-velocity air streams (Xin et al., 2012).

Another technique, called electrospinning (ES), creates ultrafine fibers with diameters ranging from nanometers to micrometers by utilizing the electrostatic repulsion between a charged polymer solution or melt and a grounded collector (Xue et al., 2017). This method is particularly useful for creating high surface area-to-volume ratio nanofibers. Electrospinning offers freedom in material selection and control over fiber morphology by enabling the manufacture of fibers from a wide spectrum of synthetic and natural polymers.

Solution blow spinning (SBS) is characterized by the use of a high-pressure gas stream in parallel to polymer solution stream. Polymer solution is forced through a nozzle rapidly, causing the solvent to evaporate and the solvent to evaporate and form micro- or nanofibers (Dadol et al., 2020). An analysis of the SBS technique, including its operational mechanisms, influential variables, and the properties of the produced fibers, will be further discussed in later sections. This in-depth analysis will showcase how SBS stands as a versatile alternative to more conventional fiber spinning methods.

1.1.2. Factors Affecting Fiber Formation

As the principles of fiber formation are often similar across different fiber production SBS, MBS, and ES, the morphology and characteristics of fibers formed by these methods are influenced by similar factors. The properties of polymers, such as concentration, viscosity, and molecular weight, significantly influence how fibers form (Theron et al., 2001). For instance, higher molecular weight polymers have been shown to increase the viscosity of the solution and so produce larger diameter fibers; finer fibers may result from lower molecular weight polymers (Parize et al. 2016). Fiber production is also significantly influenced by solvent characteristics, including solubility, volatility, and evaporation rate, as these factors determine the ease of polymer dissolution, the rate of fiber formation, and the uniformity of fiber diameter (Oliveira et al., 2014). Then, there are multiple process and instrument parameters that affect the stretching of fibers - solution temperature, nozzle design, and air pressure. Some environmental factors can also affect fiber morphology and size, e.g., humidity and temperature influence fiber formation by affecting solvent evaporation rates and polymer solidification (Chanthakulchan et al., 2015).

1.2. Solution Blow Spinning (SBS)

1.2.1. Overview

Solution blow spinning (SBS) is a straightforward and highly scalable method of creating nanofibers. This method is fairly new (among textile technologies) and has been established in just the last 15 years. In 2009, Medeiros et al. published the first report on SBS. The diameters of fibers produced ranged from 40 nm for poly(lactic acid) to several micrometers for poly(methyl methacrylate). Pressurized gas and the polymer solution are sprayed through nozzle concentric chambers in parallel streams to produce nanofibers (Figure 1). Stretching of the polymer solution in the direction of a fixed collector results from a pressure decrease and shearing at the gas/solution interface caused by the high-velocity gas under pressure. The solvent then evaporates, causing the streams of stretched polymers to form into fibers quickly. A typical SBS setup comprises a compressed gas supply, a pressure regulator, a spraying device with a concentric nozzle, and a collector.

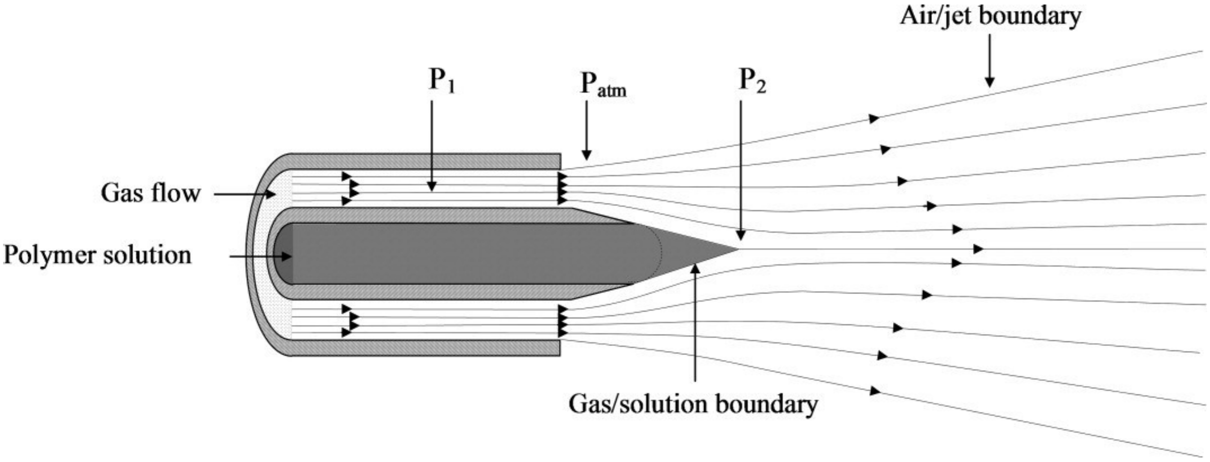

Figure 1. Figure 1: Schematic of the Solution Blow Spinning (SBS) method. (Adapted from Medeiros, Glenn, Klamczynski, Orts, & Mattoso, 2009).

SBS method offers nano- / microfiber fiber production. Because of their high porosity and small pore size, SBS-derived membranes have demonstrated potential in filtration applications like air and water purification (Tan et al., 2019). To recall fiber formation factors paragraph, the choice of polymer concentration and molecular weight not only dictates fiber size but also impacts the performance of applications such as air and water purification, where finer fibers result in enhanced filtration efficiency. Also, nanofibers are good candidates for drug delivery systems where the regulated release of drugs is needed due to their high surface area-to-volume ratio (Schuchard et al. 2021). Electrospun fibers have been used in the biomedical industry for tissue engineering applications, such as creating scaffolds for tissue regeneration and cell growth (Martins et al., 2007). The same idea can be adopted, and instead of electrospinning, fibrous polymer scaffolds for tissue engineering can be created using SBS as well (Hell et al., 2018). SBS has also been researched in the field of energy storage for creating electrode materials for batteries and supercapacitors to improve electrochemical performance and charge transfer (Yang et al., 2020).

1.2.2. Comparison with Electrospinning and Melt Blow Spinning

SBS has some similar aspects to other methods as well as contrasting aspects. Electrospinning uses electrostatic forces to pull polymer melts or solutions into fine fibers. Due to that electrospinning requires a conductive substrate or collector to facilitate fiber deposition. In contrast, SBS offers a distinct advantage: it does not necessitate a conductive substrate or any substrate at all for fiber formation. This attribute allows SBS to be particularly advantageous in scenarios where substrate compatibility or complexity is a concern, permitting more versatile and simplified fabrication processes. This characteristic will be discussed in more detail in section 1.3, which explores the direct deposition of fibers onto anchors for freestanding structures. Electrospinning has benefits like continuous fiber production, but also has drawbacks, including complicated setup requirements, low production rate, and difficulty with managing fiber morphology and alignment (Agarwal et al., 2013). Furthermore, the use of high voltages in electrospinning may limit the process's suitability for usage with specific solvents and polymers (compared to SBS) and cause problems, including uneven fiber diameters and bead formation (Huang et al. 2003). Melt blow spinning uses polymer melts and creates microfibers by extruding molten polymer through a spinneret, stretching it, and then chilling it to create fibers (Lawrence and Alexander, 2003). However, this method is limited to thermoplastic polymers and requires higher processing temperatures compared to SBS (Tan et al., 2010).

SBS exceeds melt blowing's constrained material selection and electrospinning's low production rate. The simplicity and low costs of the SBS setup are another advantage of this nanofiber fabrication technology (Dadol et al., 2020).

1.2.3. Challenges and Limitations

In an ideal scenario, SBS would yield uniform, high-quality fibers with precise control over diameter, morphology, and composition. The ideal SBS process would involve the formation of continuous, defect-free fibers with consistent properties throughout. Fibers would exhibit desired characteristics such as high aspect ratio, surface area, and mechanical strength, making them suitable for various applications. The process would be highly scalable and reproducible, allowing for the mass production of fibers with minimal variability across batches. However, in real life experimentation there are a few limitations. Achieving constant fiber morphology and constant diameter is one of the main problems, mainly when working with different polymer solutions and varied processing conditions. This characteristic is a primary concern in some fields like filtration, where constant and homologous distribution is important for proper performance. Differences in fiber quality and performance might result from environmental conditions, processing parameters, and polymer-solvent characteristics (Medeiros et al., 2009). This issue is not tied just to the SBS method and can be seen in other described methods as well. Furthermore, issues remain with the SBS process's scalability for large-scale manufacturing, especially when preserving consistent fiber qualities and production efficiency (Zhang et al., 2005). An additional constraint associated with the SBS procedure is the potential for bundled fiber development as a result of insufficiently regulated gas flow. The non-homogeneous fiber distribution that these bundles may produce could lead to poor performances in specific fields such as filtration, where uniformity is crucial for proper function (Dias et al., 2020). However, for applications involving freestanding structures, this hierarchical structure can be advantageous. The bundled fibers can provide enhanced support and structural integrity, making the material more suitable for applications requiring robust mechanical properties.

1.3. Unsupported Solution Blow Spinning

Even though SBS is a versatile and widely used process for producing micro- / nanofibers, most current research concentrates on mat collection instead of direct deposit of the fibers as free-standing structures. For example, studies like those by Medeiros et al. (2009) focus primarily on using SBS to fabricate nanofiber mats. Mats can be collected post SBS deposition and then unsupported freestanding structures can be constructed. Noel et al.'s (2019) research highlights SBS's applicability in producing fibrous membranes for air filtration, highlighting the common practice of generating nanofiber mats for later use in the construction of free-standing structures. This tendency indicates that present research efforts tend to concentrate on using SBS-produced mats as building blocks for further fabrication procedures, even though SBS offers excellent potential for direct deposition of free-standing unsupported fiber structures. However, recent advancements have shown promising developments in the creation of three-dimensional micro-nanofiber structures using SBS. A novel SBS device capable of fabricating such structures was recently introduced, opening new possibilities for direct deposition of free-standing unsupported fiber structures (Liang et al. 2017). Even with these developments, there are still no extensive studies in the literature on the direct deposition of free-standing structures using SBS.

It is essential to recognize that various applications impose different demands on the fiber structures. Strict uniformity in fiber distribution, for example, is required for applications in fields like filtering; however, this need could not easily translate to robotics or other fields where adaptation and flexibility are critical. Because the requirements and objectives of the processes involved in the fabrication of mats and the spinning of unsupported structures using SBS can vary, it is not sufficient to simply reproduce current methodologies in the transition. Furthermore, this alteration brings in the physical aspect of post-tensioning, which is minimized or not causing significance other that a reduced products material area in mat manufacturing, but is crucial for creating freestanding constructions as it can break the fibers. The requirement for post-tensioning highlights a significant methodological separation, posing a research, which offers a chance for more research in this field and finding new applications for the SBS method in different fields.

1.4. Scaffold Fabrication with Freestanding Structures via SBS

Studies demonstrate that cryogenically aided SBS can produce porous bioactive nanofibers that can be shaped into 3D macroporous scaffolds (Medeiros et al. 2016). This technique highlights how versatile SBS is in creating scaffolds that resemble the extracellular matrix, which is essential for promoting tissue regeneration and cell proliferation. Furthermore, Simbara et al. (2019) compare aligned and nonaligned poly (ε-caprolactone) fibrous scaffolds prepared via SBS, highlighting how the orientation of fibers within these mats can influence cellular behavior, thereby affecting the overall efficacy of the scaffolds in tissue engineering applications. To create composite materials that enable bone regeneration, Popkov et al. (2021) investigate the SBS manufacture of PLLA/hydroxyapatite composite scaffolds for bone tissue engineering. The direct integration of bioactive elements into these scaffolds offers an additional strategy for improving scaffold performance. The direct spinning of unsupported structures via SBS could offer significant benefits, including reduced production complexity, improved scaffold architecture, and enhanced mimicry of natural tissue structures.

2. METHODS

2.1. Materials

The primary polymer used in the nanofiber fabrication was poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) from Aldrich with Mw ~43,000 g/mol. PVDF-HFP was a suitable candidate for examining nanofibers' structural integrity and post-tensioning behavior. 14% w/v PVDF-HFP polymer solution was prepared by dissolving 4g in 26 mL of 4-methyl-2-pentanone (MP) and adding 2g of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (IL) from Solvionic with 99.5% purity and Mw 260.24 g/mol. 1-1.2 bar pressure was used in SBS process for PVDF-HFP solutions.

Polyethylene oxide (PEO) was also employed as a secondary polymer to draw comparisons with the PVDF-HFP fibers. PEO from Alfa Aesar with ≤100% purity and Mw ~1000,000 g/mol was selected for its water solubility and compatibility with SBS. Two solvents were used for PEO: water (H_2O) and MP. Both solutions were prepared at 29% w/v. For solution with MP 1-1.2 bar pressure was used for spinning, for H_2O solution 0.5 bar pressure was used. The MP solvent was utilized across all polymer solutions, allowing a comparative analysis of the fibers under the same solvent conditions.

2.2. Solution Blow Spinning Setup

The SBS system, depicted in Figure 2A, was used for all fiber depositions in this work. The setup consists of a pressurized gas tank connected to a pressure gauge and then via tubing to an SBS apparatus with a solution reservoir. Instead of a gas tank compressed dry air was used as the working gas. The solution reservoir is part of a conventional airbrush, as shown in Figure 2B, which serves as the core of our spinning apparatus. An improvement over the standard airbrush design is incorporating a heating coil supplied by a DC power source. Heating coil was made of a 1.5 meter long 0.2 mm diameter copper wire coated with enamel and textile isolation layer. The wire was coiled around the tip and reservoir of the airbrush (Figure 2A). This addition solves the frequent problem of the polymer solution becoming trapped in the airbrush canal as it cools during the deposition process, blocking further deposition. A steady and continuous flow of the polymer solution through the nozzle is ensured by keeping the solution at an elevated temperature. The airbrush was kept at 60-65°C. Using a heating coil, the airbrush was kept from clogging, and the process of creating fibers was smoother and more consistent. This adaptation was essential for achieving a steady production of fibers.

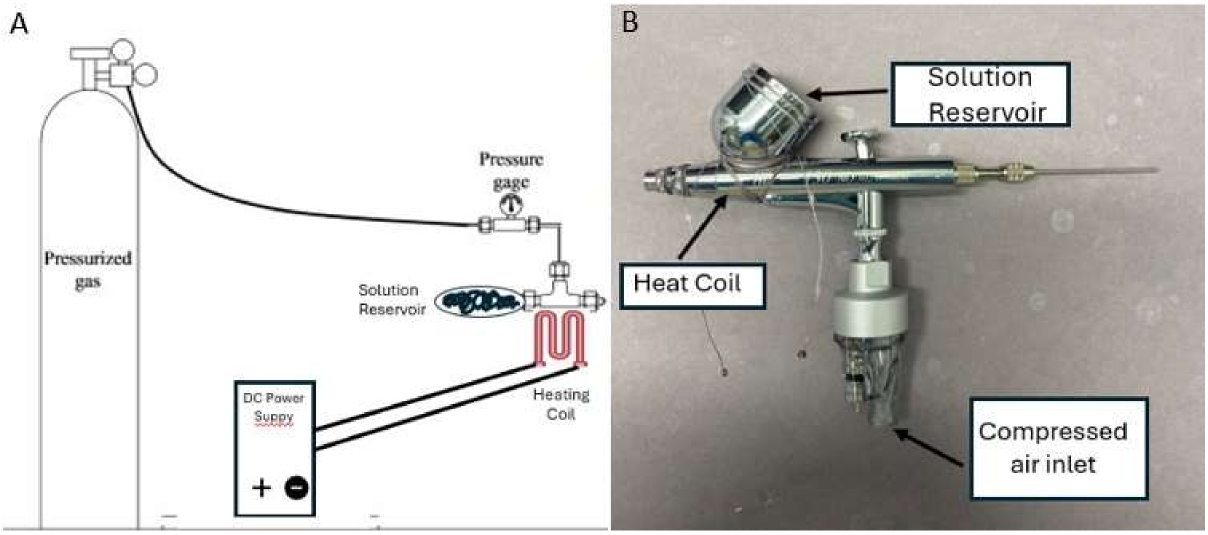

Figure 2. Solution Blow Spinning Setup. (A) Schematic of the SBS setup (Adapted and modified from Medeiros, Glenn, Klamczynski, Orts, & Mattoso, 2009). (B) Detailed view of the airbrush serving as the core of the spinning apparatus.

2.2.1. Custom Made SBS Apparatus

In addition to the standard SBS apparatus used in previous experiments, a new SBS apparatus was constructed (Figure 3).

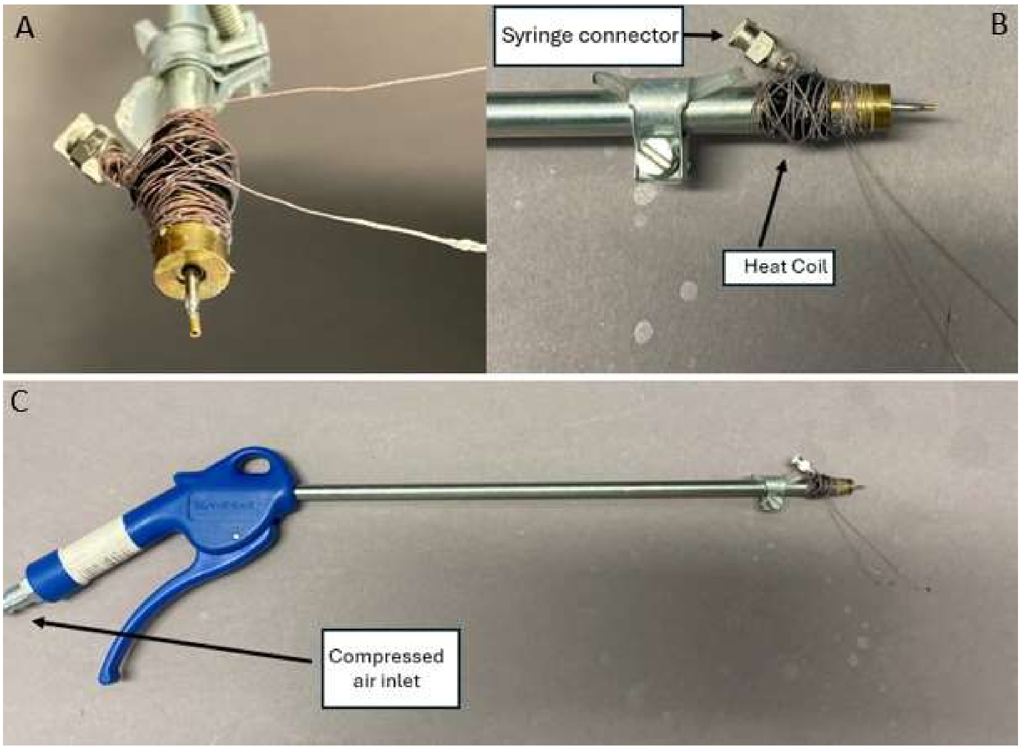

Figure 3. Custom-made Solution Blow Spinning (SBS) apparatus inspired by Santos et al. (2016).

This device was inspired by the design described in the study by Santos et al., 2016, which details a highly effective configuration for fiber production. The construction of our custom SBS apparatus replicated the dimensions of the nozzle opening as specified in the referenced paper (Figure 4). Compared to the referenced design, we switched the Bunsen burner to a heating coil to provide more controlled heating conditions. The design also accommodates the future addition of a syringe pump, which would enable more controlled experiments with a controlled solution delivery rate.

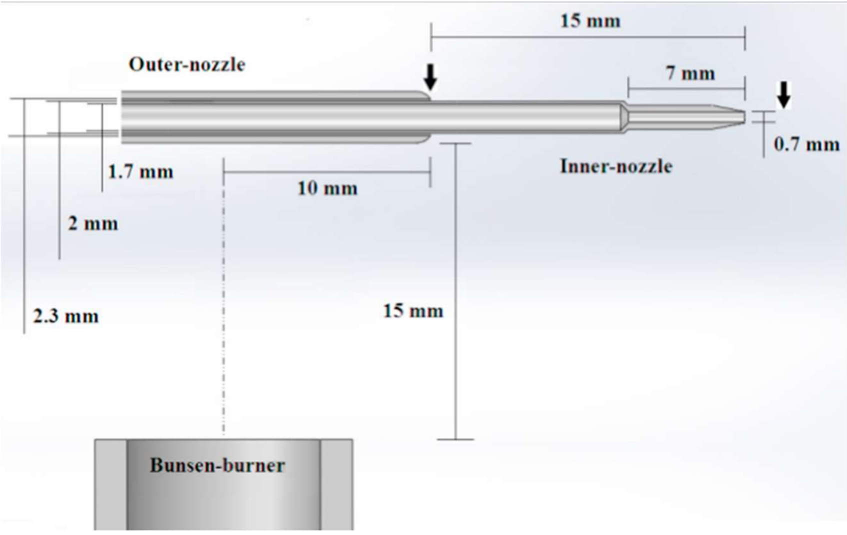

Figure 4. Dimensions and nozzle design used for the custom Solution Blow Spinning (SBS) apparatus. (Adapted from Santos, Medeiros, Blaker, & Medeiros, 2016).

2.3. Analysis Methods

2.3.1. Scanning Electron Microscopy (SEM) Observations

To ensure that the micrographs obtained would be representative of the fibers' intrinsic shape and free of substrate-induced artifacts, samples for SEM examination were carefully removed from the center of unsupported sections of the fiber structures. Before imaging, the samples were held in a vacuum chamber, which effectively eliminated moisture and prepared the samples for further sputter coating process. Following this, the samples were uniformly coated with a thin, 5-nanometer layer of gold using a LEICA EM ACE600 sputter coater. This conductive coating's application increased the SEM pictures' clarity and allowed for the precise imaging of the nanofibrous structures.

Scanning electron microscopy (SEM) was used to characterize the morphology of the nanofibers produced by the SBS method. A Hitachi TM3000 microscope was used for analysis, operating in analytical (EDX) mode to obtain detailed micrographs of the fibers.

2.3.2. Post-Tensioning

The post-tensioning experiments were conducted using a custom-built apparatus, as depicted in Figure 5. Polylactic Acid (PLA) was chosen for the attachment points in post-tensioning tests as it is a material that is easily accessible and widely utilized in 3D printing. PLA constructions provided a consistent and repeatable attachment medium as anchoring points within the post-tensioning apparatus. The setup includes area (4x5cm) for polymer deposition where the nano/microfibers are collected. A force sensor is installed at one end of the apparatus to monitor the force applied to apparatus by contraction of the polymer fibers. This sensor is interfaced with LabVIEW software, which records force data in real time, ensuring tension measurement during fiber formation and post-tensioning after fiber formation is done.

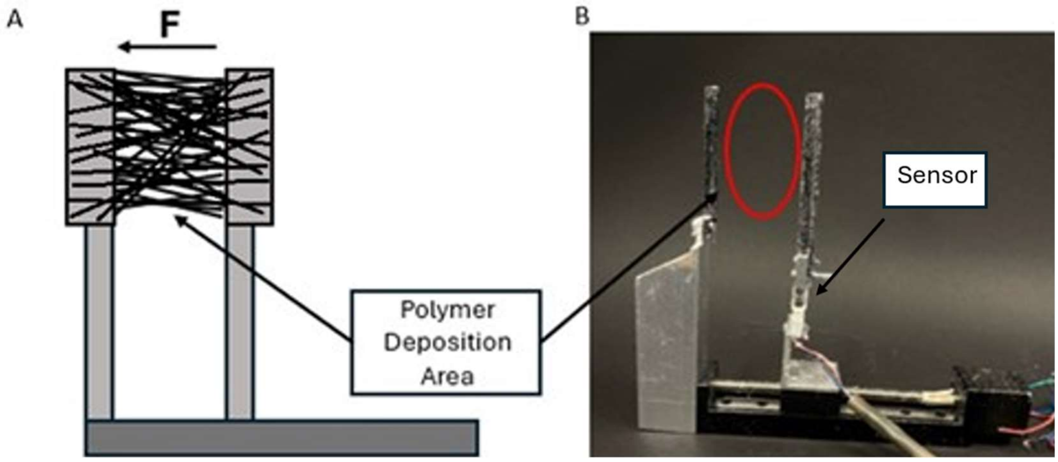

Figure 5. Custom-built apparatus for post-tensioning experiments

The polymer spinning process is executed in three distinct phases over a total duration of 90 seconds. The initial phase involves a direct application for 30 seconds, where the spinning jet is aligned in parallel (0-degree angle) to the post-tensioning apparatus. This is followed by two oblique spinning phases, 30 seconds each from the left and right sides, at a 45-degree angle to the polymer deposition area, to ensure even coverage and fiber entanglement.

2.3.3. T-Peel Test

For the evaluation of adhesion properties of the sprayed fiber solutions, the "T-Peel Test" was conducted with a setup as illustrated in Figure 6. Polytetrafluoroethylene (PTFE) was the substrate used for the T-Peel adhesion tests. In this test, nano/microfibers were sprayed using SBS between two PTFE plates to create an unsupported structure. PTFE was specifically selected as a test substrate because of its low surface energy, which generally impedes adhesive bonding to evaluate the adhesive properties of the fiber solutions. After the spinning process, the unsupported section of the fibrous structure between the PTFE plates was cut in half, leaving a small portion of the fibers hanging from one of the plates. This protruding fiber segment was then clamped securely in the AEL-A-10 Motorized Test

Stand equipped with a force sensor. The PTFE plate remained stationary at the base while the clamp, moving upwards, applied tension to the fiber structure until it detached from the PTFE surface. The sensor, recorded the force exerted in real-time, measuring the peel strength of the fibers. The detachment point, when the fiber structure became detached from the PTFE plate, was noted as the critical point, reflecting the adhesive strength of the fiber solution.

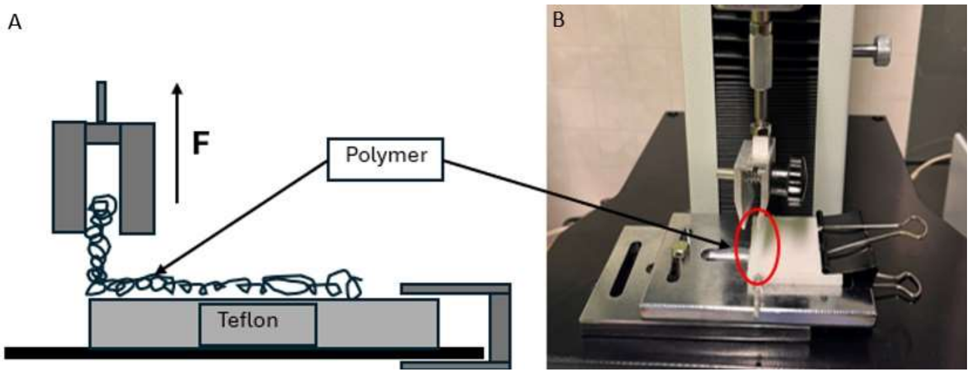

Figure 6. T-Peel Test setup for evaluating the adhesion properties of sprayed fiber solutions. (A) Schematic of the test setup. (B) The motorized test stand equipped with a force sensor to measure the peel strength.

3. RESULTS AND DISCUSSION

3.1. Custom Built Apparatus performance

Regarding overall efficiency and convenience of use, the custom SBS apparatus did not outperform our regular apparatus. While it was capable of producing fibers that were structurally similar to those produced by the original apparatus, we encountered significant practical challenges. The fact that the apparatus could not be disassembled like the original one made cleaning it time-consuming and challenging, which was one of the primary problems. The device frequently clogged, which made it difficult for us to carry out experiments without having to stop for maintenance. These problems were created by the specific polymer solutions used, which tended to solidify quickly upon cooling, leading to frequent blockages in the nozzle and internal channels. Despite these challenges, the custom-built apparatus remains valuable for future studies. One notable benefit that remains relevant is the ease of integration of a syringe pump, which provides accurate control over the polymer solution's flow rate. This might be especially helpful when dealing with polymer solutions that solidify more slowly, thereby reducing the clogging problems we encountered.

3.2. Unsupported Structures (Bridging)

In the first attempt to create unsupported structures, small copper mesh substrates were sprayed with a PVDF-HFP/MP solution using the SBS method. The mesh allowed for the investigation of fiber bridging capabilities on a small scale. Subsequent experiments scaled up the complexity and size of the structures. These samples' SEM analysis showed the development of miniature, unsupported structures in the center of the mesh cells, with each cell's edges serving as the structure's anchors or supports (Figure 7).

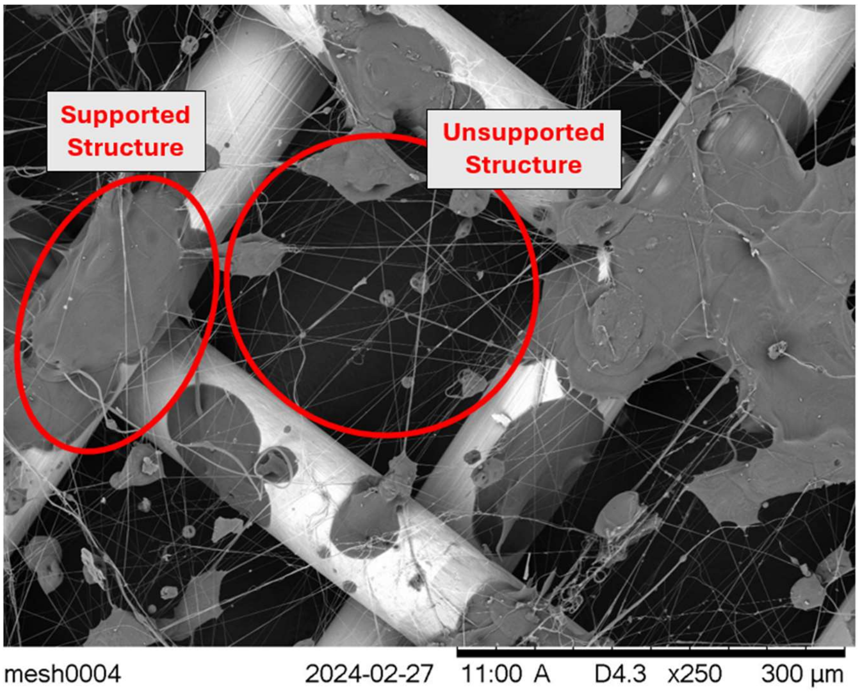

Figure 7. Scanning Electron Micrograph of Nanofiber Formation on Copper Mesh Substrate. The SEM micrograph illustrate the initial development of miniature unsupported structures within the mesh cells.

Despite their small size, they provided first insights into unsupported structures as well as the potential for scaling up this approach to create larger unsupported structures. Following that, using nanofibers sprayed from the SBS setup, the experimental focus shifted to creating bridges between two plexiglass panels. Acrylic plastic (plexiglass) was used to create brackets for larger unsupported structures. This material's accessibility and machinability made it an ideal candidate for assessing the fibers' bridging potential over more significant gaps. The spacing between the plates in this arrangement was increased to 4 cm, which is far more than the milimeter-scale gaps in the copper mesh experiment. The fibers were able to create a bridge across the plates without collapsing despite the wider distance and the reduced count of anchors/support beams (see Figure 8). This practical example demonstrates the approach's scalability and potential to build larger unsupported structures.

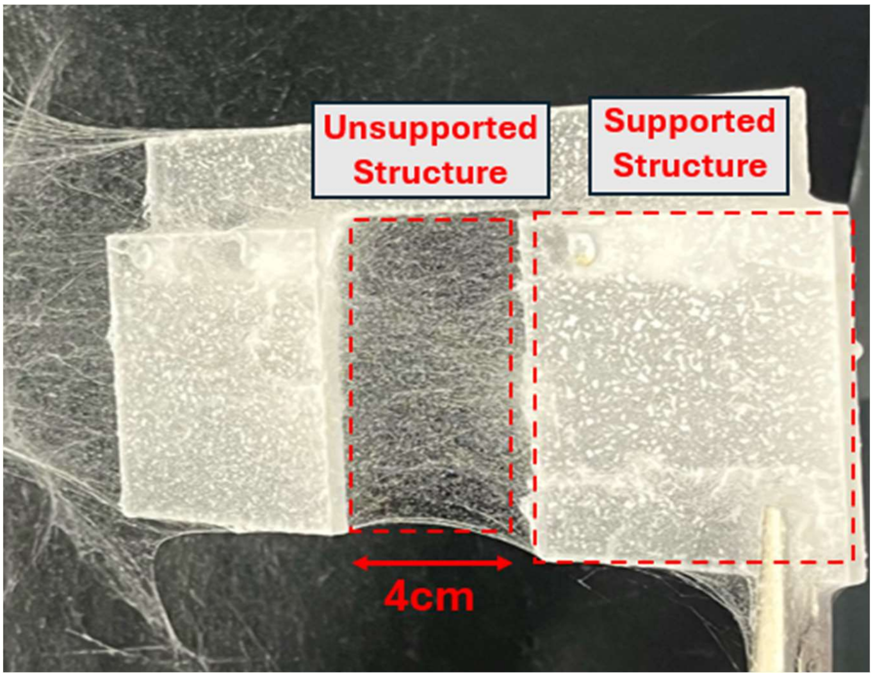

Figure 8. Nanofiber bridges created between two plexiglass panels using Solution Blow Spinning. The fibers successfully span a 4 cm gap, demonstrating the scalability and potential for creating larger unsupported structures.

3.3 Fiber Morphology

The SEM analysis of the fabricated nanofibers reveals distinctive morphological characteristics influenced by the choice of polymer solution and the incorporation of additives. SEM micrographs obtained from different polymer solutions (Table 1) provide insights into the fiber structure and organization. All of the samples used for SEM imaging were obtained from unsupported structures.

The SEM micrographs of nanofibers produced from different polymer solutions show distinct morphologies, with merging behavior, and overall structural organization. Nodules in fiber networks are typically defined as localized thickening where fibers intersect and fuse, forming robust points that potentially enhance the mechanical integrity of the network. Fiber thickness, or the diameter of individual fibers, is an important factor influencing the mechanical strength and flexibility of the resulting fibers. Measurements of fibers obtained from SEM micrographs present a diverse range of thicknesses (Table 1).

ABBREVIATION	POLYMER	SOLVENT	ADDITIVES	CONCENTRATION	FIBER THICKNESS
PVDF-HFP/MP	Poly(vinylidene fluoride-co-hexafluoropropylene)	4-methyl-2-pentanone	-	14 w/v%	0.8 μm
PVDF-HFP/MP + IL	Poly(vinylidene fluoride-co-hexafluoropropylene)	4-methyl-2-pentanone	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	14 w/v%	1.2 μm
PEO/MP	Polyethylene oxide	4-methyl-2-pentanone	-	29 w/v%	1.9 - 18.1 μm
PEO/H_2O	Polyethylene oxide	Water	-	29 w/v%	0.4 μm

TABLE 1. Characteristics of nanofibers produced from different polymer solutions, as observed from SEM micrographs.

These variations suggest that the solvent and additives play crucial roles in defining the structural parameters of the fibers.

3.3.1 Morphological Patterns of PVDF-HFP Based Fibers

PVDF-HFP with plasticizer SEM micrographs shows a mesh with a significant degree of merging and interlinking, as well as the formation of nodules where the fibers intersect. The structure suggests a dense network with fibers and nodules distributed throughout the matrix (Figure 9A).

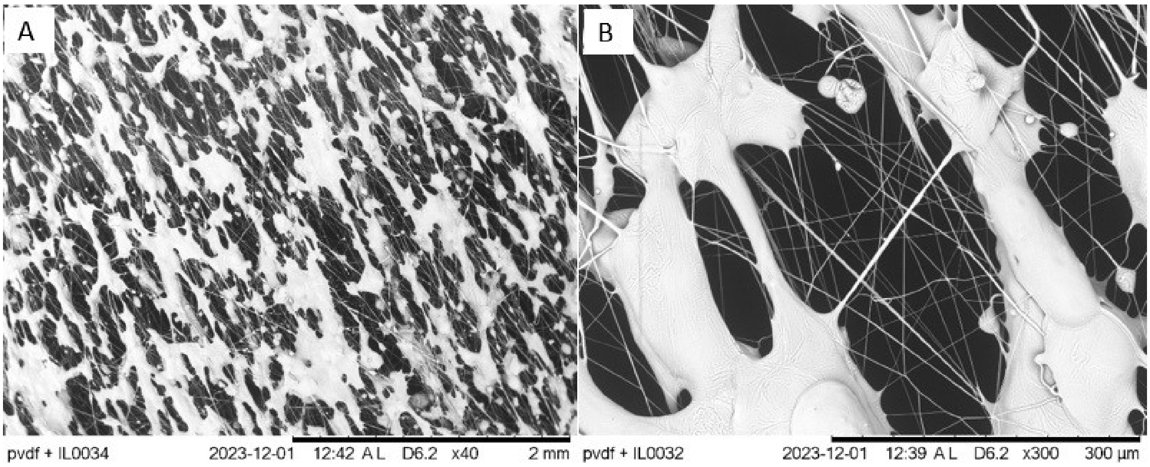

Figure 9. SEM Micrographs of PVDF-HFP / MP with Ionic Liquid Based Nanofibers. (A) Overview of the dense fiber network with significant merging and interlinking. (B)

Higher magnification showing individual fibers with varying diameters and pronounced nodules, indicating high interaction between fibers facilitated by the ionic liquid.
The higher magnification offers a closer look at individual fibers (Figure 9B). We can see that the fibers vary in diameter, with some areas appearing thickened due to the fusion of fibers. The nodules appear more pronounced, suggesting a high level of interaction between fibers, possibly facilitated by the ionic liquid. In the SEM micrographs of PVDF-HFP / MP without ionic liquid the fibers appear more individualized and less interconnected compared to those with ionic liquid (Figure 10).

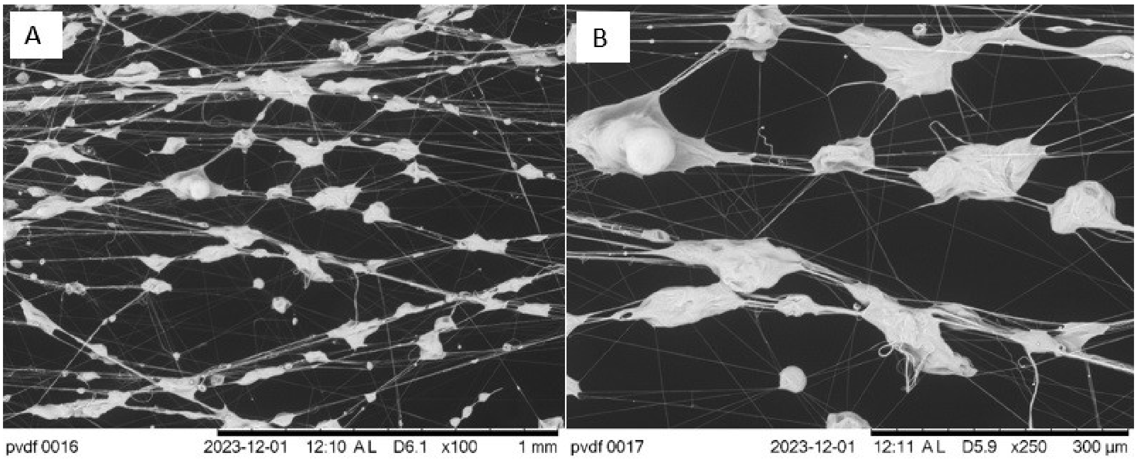

Figure 10. SEM Micrographs of PVDF-HFP / MP Based Nanofibers. The fibers appear more individualized and a more uniform with fewer irregularities compared to those with ionic liquid, but still showing evident merging into nodules or merged fibers, but to a smaller degree.

There is less evidence of nodules or merged fibers, suggesting less entanglement and fusion of the polymer and the distribution of fibers seems more uniform, with less variability in diameter and fewer irregularities. There are slight variations in fiber morphology when comparing the SEM pictures of PVDF-HFP / MP solutions with and without the addition of an ionic liquid additive. The lack of ionic liquid appears to result in a more homogenous fiber network with smaller fiber diameter (0.8 μm) and less merging of the fibers. This could suggest that the ionic affects fiber production process. IL impact on fiber morphology is profound; it not only affects the thickness and uniformity of fibers but also enhances the formation of nodules. By slowing the evaporation process due to interaction with solvent, ionic liquids allow more time for the polymers to entangle and fuse, promoting the formation of structurally complex fiber networks. These networks are complex due to features such as increased fiber interconnectivity, varying fiber diameters, and the presence of nodules. This behavior is beneficial in creating fiber structures with hierarchical distribution that could potentially lead to higher structural integrity.

3.3.2 Morphological Patterns of PEO Based Fibers

Notably, the PEO/MP solution's SEM micrographs show fibers that are thicker in diameter than those of other solutions, along with a noticeable merging and interlinking of fibers that results in the formation of large, linked nodules (Figure 11).

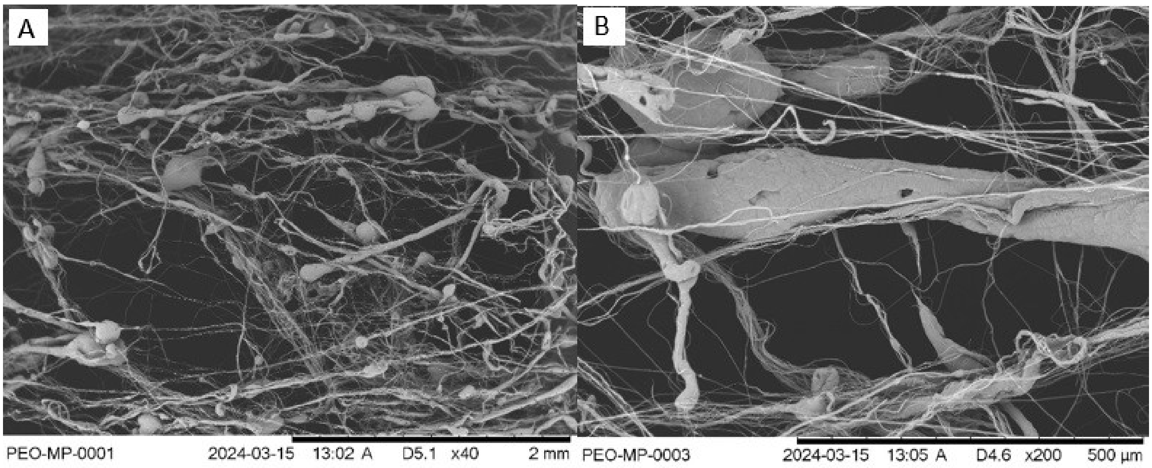

Figure 11. SEM Micrographs of PEO/MP Based Nanofibers. (A) Low magnification view showing the overall structure with thick fibers and significant merging. (B) Higher magnification revealing large, linked nodules formed by the interlinking of fibers.

This phenomenon suggests a higher propensity for polymer entanglement and fusion within the PEO/MP solution, resulting in the observed structural complexities. In contrast, the SEM micrographs of the PEO/ H_2O solution show fibers with smaller diameters and less merging, which suggests that individual fibers are distributed more uniformly and that there is less interlinking between neighbouring fibers (Figure 12). This difference in the morphology of the fibers between PEO/MP and PEO H_2O solutions highlights the vital role that solvent composition plays in fiber formation and structural organization.

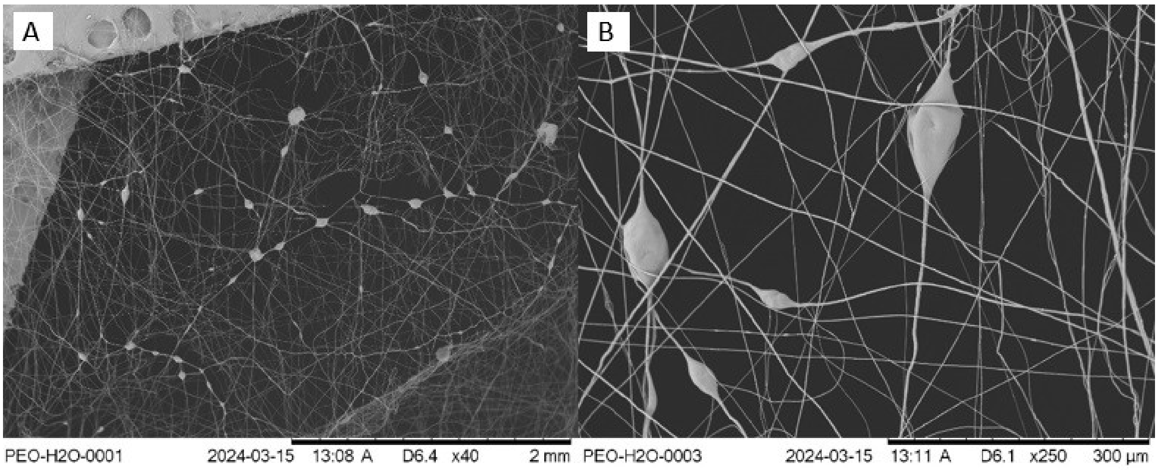

Figure 12. SEM Micrographs of PEO/ H_2O Based Nanofibers. (A) Low magnification view showing the overall structure with thinner fibers and more uniform distribution. (B) Higher magnification revealing more individualized fiber network.

Interestingly, the directionality of the fibers looks less consistent and aligned in all of the SEMs than expected, with a randomized orientation that includes orientations fully perpendicular and parallel to the spinning direction in all of the samples. This was unexpected because the spinning process typically induces a certain degree of alignment due to the directional force applied during fiber extrusion. The gas jet in SBS is supposed to align fibers in the direction of the airflow, creating a more ordered structure. However, the observed random orientation suggests that other factors, such as turbulent airflow or variations in the polymer solution, might be influencing the fiber deposition.

3.3.3 Morphological Aspects of SBS on Planar Substrates

When polymer solutions are sprayed by SBS directly onto the planar substrate, they form a film-like structure, with only some fiber characteristics retained. This phenomenon occurs because the planar substrate provides a continuous surface that encourages the polymer to spread out and form a more cohesive film rather than discrete fibers. The resulting material resembles a thin film with embedded fiber-like features SEM analysis of PVDF-HFP / MP films, with and without the ionic liquid additive, confirms the formation of continuous film structures on the substrate (Figure 13A and B). These films exhibit a smooth surface with embedded fibrous textures, indicating that while the overall morphology is film-like, some nano/micro scale fiber characteristics persist. Notably, any gaps or voids within the film are filled with fiber morphology structures similar to SEMs from unsupported parts of the fiber structure (Figure 13C and D).

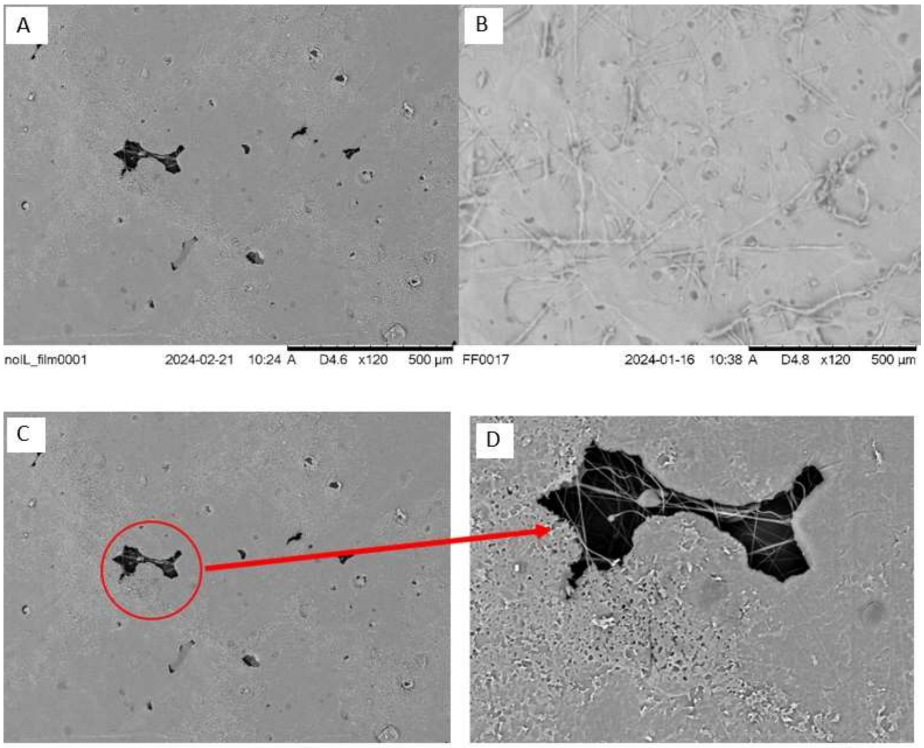

Figure 13. Comparison of SEM Micrographs for PVDF-HFP Based Film Structures. (A) Continuous film structure formed on the substrate without ionic liquid, showing smooth surface and embedded fibrous textures. (B) Continuous film structure with ionic liquid, exhibiting similar smooth surface but with more pronounced fibrous features. (C and D) Close-up view of gaps or voids within the film filled with fiber morphology structures, similar to those observed in unsupported fiber structures.

3.4 Post-Tensioning

Post-tensioning is one of the defining mechanisms that control the functional features of the fibers after deposition and before final state. Internal tensions arise during the SBS process as the sprayed polymer solution changes from a fluid to a fibrous, hardened state. If retained as residual tension within the fiber structure, these stresses can influence the fiber's volume, or fiber length and adaptability to external forces. It is essential to comprehend post-tensioning behavior to predict how well nanofibrous materials can perform in real-world applications. For example, in biomedical applications, the post-tensioning degree may impact tissue scaffold compatibility with the dynamic biological environment by exerting force on the underlying tissue, which can influence cell behaviour, attachment, and proliferation. . Similarly, the durability and efficiency of nanofiber meshes in filtration and environmental applications are determined by their mechanical integrity, which could be attributed to post-tensioning.

3.4.1 Post-tensioning in PEO Fibers

3.4.1.1 Mechanical and Visual Implications

The appearance of PEO/MP fibers can be described as not adequately tensioned, resulting in a material with visually loose and slack fiber formations (Figure 14). which makes the material unsuitable for use in tensile integrity-requiring applications. Unsupported structures rely on the tension in the fibers to hold them together and provide a foundation for the addition of further structural or functional components. Furthermore, these structures are dependent on the internal tension of fibers to maintain structural integrity; this internal tension allows the structure to withstand external forces, including airflow which could cause the fibers to move or break if not properly tensioned.

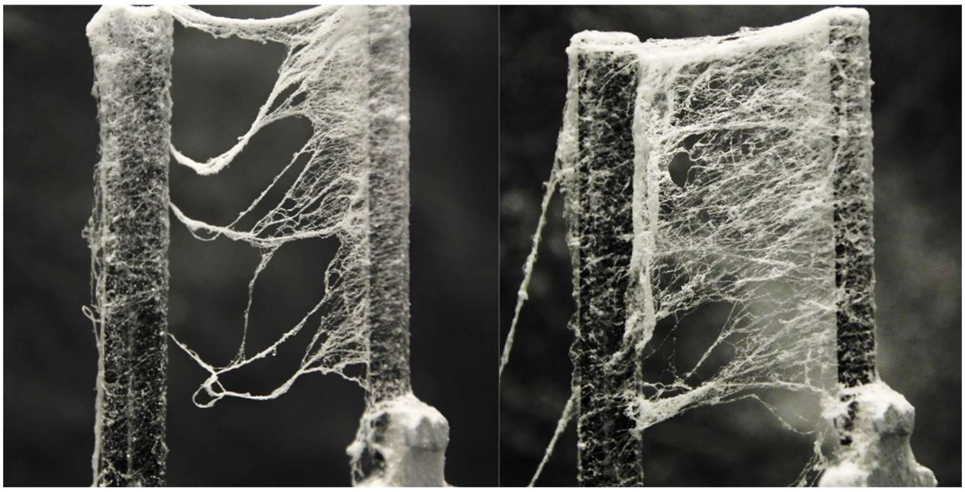

Figure 14. Visual appearance of PEO/MP fibers indicating inadequate tensioning.

In the case of PEO/ H_2O fibers, the design of such structures is limited by the fibers ability to withstand its own post -tensioning forces without breaking apart (Figure 15). SBS-produced fibers from PEO/ H_2O fail to comply with post-tensioning requirements needed to work with complicated unsupported structures.

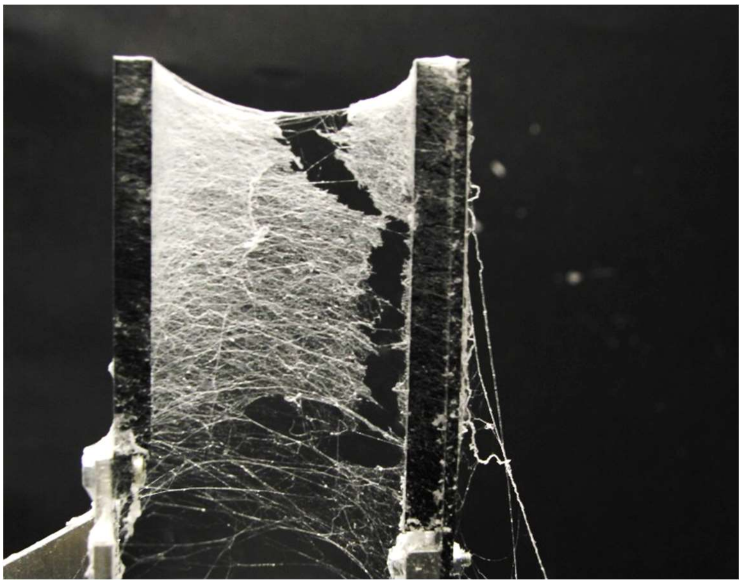

Figure 15. Visual appearance of PEO/MP fibers in Post-Tensioning Experiment

3.4.1.2 Post-tensioning dynamics of PEO/ H2O and PEO/MP Solutions

There was little post-tensioning activity in the PEO/ H_2O fibers (Figure 11). Interestingly, most trials showed that the PEO/ H_2O fibers ruptured because they reached an elongation threshold beyond which they could not withstand the applied tension. This cutoff represents a crucial moment where the fibers go from a potentially useful (tensioned) state for unsupported structures to a failing state. When used in applications where the fibers have to cross gaps or create complex three-dimensional structures, their capacity to bear a specific amount of self- and outside tension without breaking is critical to their functionality. PEO/ H_2O deposited fibers made up the smallest deposited weight. As seen in Figure 16, the deposited weight is small compared to PEO/MP weight (Figure 17). Therefore, an extra SBS trial with longer deposition time (240s) was performed, to show that with prolonged spinning time, higher weight can be achieved. Even though a higher weight was achieved (comparable to PEO/MP deposited weights), that did not change the overall tensioning profile of fibers (Figure 16).

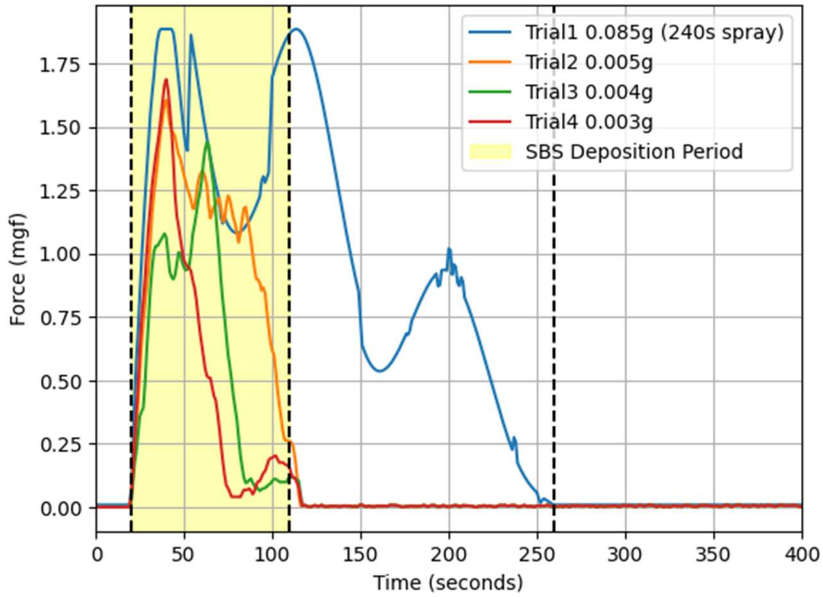

Figure 16. Tensioning profile and deposited weight of PEO/ H_2O fibers. The fibers exhibit low deposited weight and minimal post-tensioning activity, highlighting their inability to maintain tension.

Although PEO/MP fibers did not retain tension after SBS, they exhibited greater post-tensioning forces (Figure 17). When the spinning stopped, the fibers rapidly reverted to a relaxed state with no more tensioning forces, with fibers being stretched longer then deposition area. In visual terms, the fibers took on a relaxed position, with no visible tension, indicating an equilibrium state in which no significant forces were applied to the sensor. This behavior suggests that the fibers did not experience the internal pressures after deposition commonly associated with post-tensioning, even though they did accomplish physical elongation and tensioning during spinning time. This behavior is contradictory to the requirements for building unsupported structures. Such structures mandate a degree of inherent tension within the fibers to maintain structural integrity and form. Without post-tensioning, fibers may still entangle with supports, but they will not tauten the structure. While a non-taut structure could also be stable, it may lack the necessary rigidity and mechanical stability required for certain three-dimensional scaffold formations or unsupported path creation.

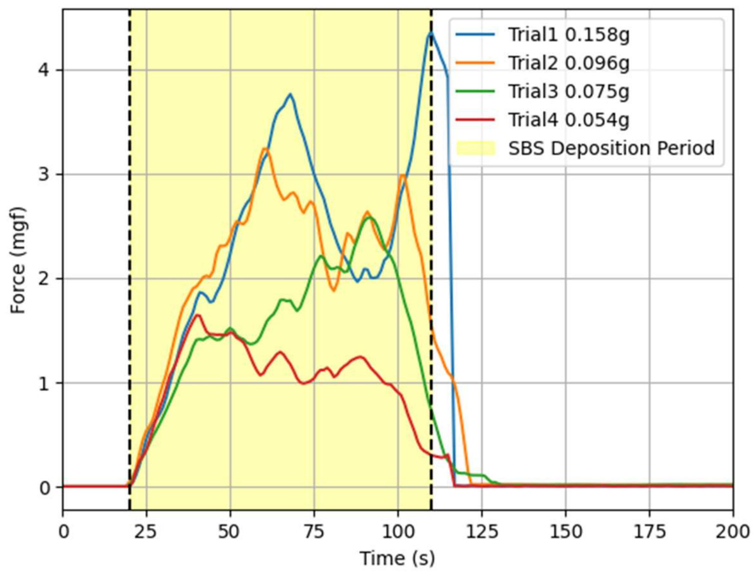

Figure 17. Post-tensioning profile of PEO/MP fibers. The fibers demonstrate greater post-tensioning forces compared to PEO/ H_2O fibers, although they do not retain tension after the spinning process.

When comparing two different solvents involved in PEO solutions in this experiment, neither of them exhibit any post-tensioning force (Figure 18). However, they exhibited different fiber morphology and peak forces.

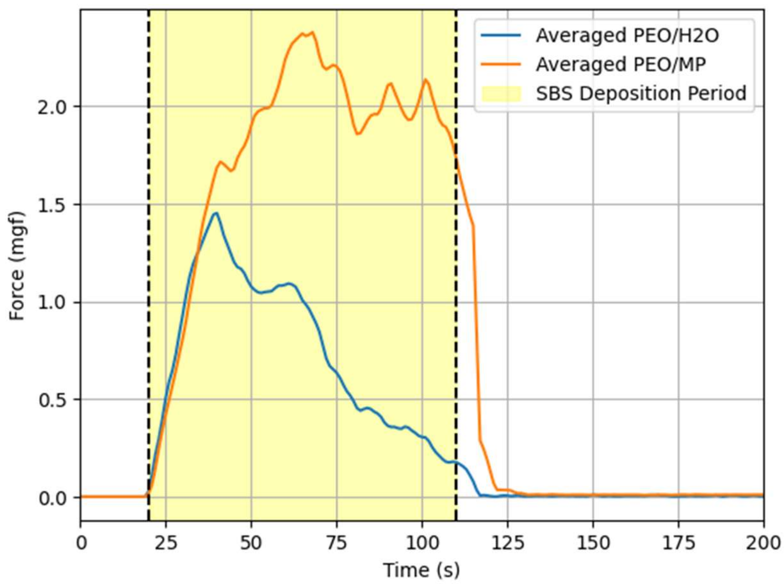

Figure 18. Comparison of post-tensioning behavior in PEO fibers using different solvents. The fibers exhibit varying peak forces, but neither PEO/ H_2O nor PEO/MP solutions show significant post-tensioning forces.

3.4.2 Post-tensioning in PVDF-HFP Fibers

3.4.2.1 Post-tensioning dynamics of PVDF-HFP / MP based nanofibers

PVDF-HFP fibers exhibit a characteristic tensioning curve immediately following the SBS process (Figure 19A). The initial spike in tension is associated with the polymer's fast phase transition from liquid to solid; post-tensioning continues for a short time after spinning stops and reaches a threshold at which the fibers can no longer withstand the tension and begin to rupture, as a result, the curve descends. Even yet, there is still stress applied to the sensor by several fibers, and the plateau shows that the fiber structure has stabilized as it approaches equilibrium. This tendency is supported by the normalized data in Figure 19B, which shows a similar behaviour of post-tensioning aspect attained across trials. The overall trend is similar to tensioning trends from PEO experiments, but with some post-tensioning present (Figure 18). However, in comparison to PEO the forces exerted are much higher, and on most trials the forces retained after end of SBS are higher than peak forces of any of the PEO trials. PVDF-HFP seems to be more suitable for unsupported structures due to retaining some of the tension. The issue is that post spinning, the fibers are not able to withstand their own tension and start to break, dropping the force values down to half of the peak. This effect is not beneficial as a lot of fibers are breaking, therefore structural integrity is affected.

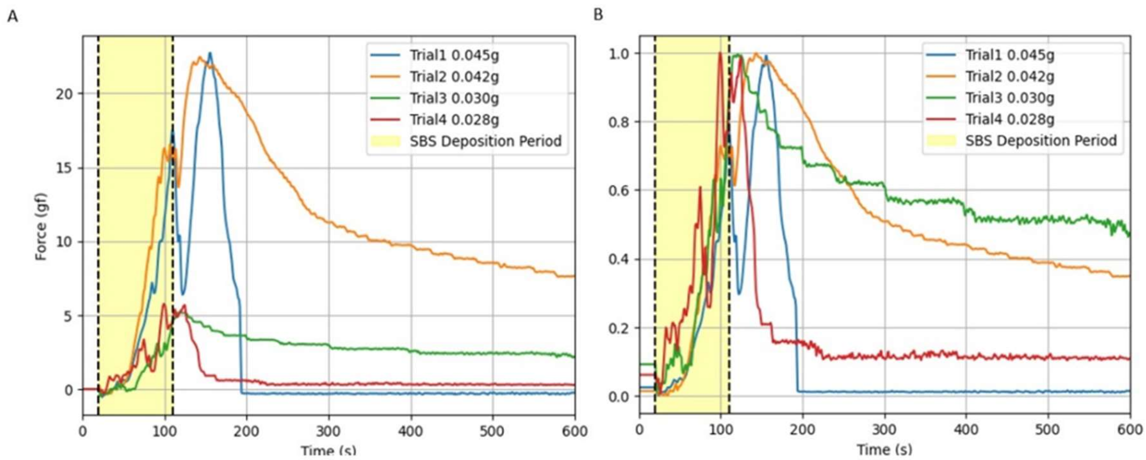

Figure 19. Post-tensioning dynamics of PVDF-HFP/MP nanofibers. (A) Tensioning curve showing an initial spike in tension followed by decrease as fibers rupture. (B) Normalized data illustrating a trend of post-tensioning behavior across trials.

3.4.2.2 Enhanced Post-Tensioning with Ionic Liquid

When ionic liquid is incorporated into the PVDF-HFP polymer solution, a significantly different post-tensioning profile is observed. Figures 20A and 20B demonstrate a high-tension state that lasts even after spinning time ends, as well as tension rising after the SBS process concludes, suggesting that the ionic liquid has a significant effect on the fiber production process. The ionic liquid functions as an inhibitor, slowing down the pace at which the solvent evaporates and acting as a plasticizer to give the fibers flexibility. This prolongs the window of time for fiber production and alignment.

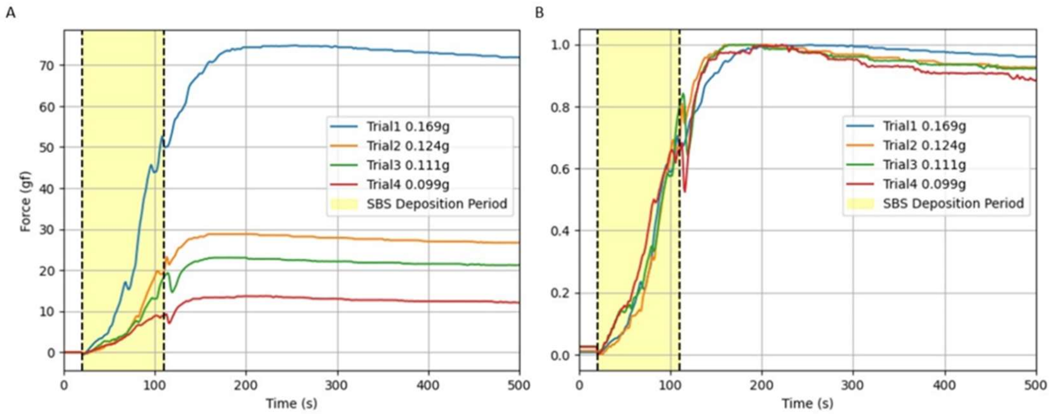

Figure 20. Post-tensioning dynamics of PVDF-HFP/MP + IL nanofibers. (A) Tensioning curve showing sustained high-tension state after spinning concludes across trials. (B) Normalized data illustrating a trend of post-tensioning behavior across trials.

Presence of ionic liquid is characterized by a sustained tensioning curve that plateaus close to peak force values, which is a desirable trait for fibers intended for use in creation of unsupported structures. A significant difference in tensioning curve can be observed when comparing results from non-ionic liquid solution and ionic liquid solution (Figure 21). The observed results provide insight in the importance of the ionic liquid's dual function. Its plasticizing effect is thought to reduce internal stresses and enhance fiber flexibility, while its evaporation inhibition could lead to a more controlled fiber solidification process.

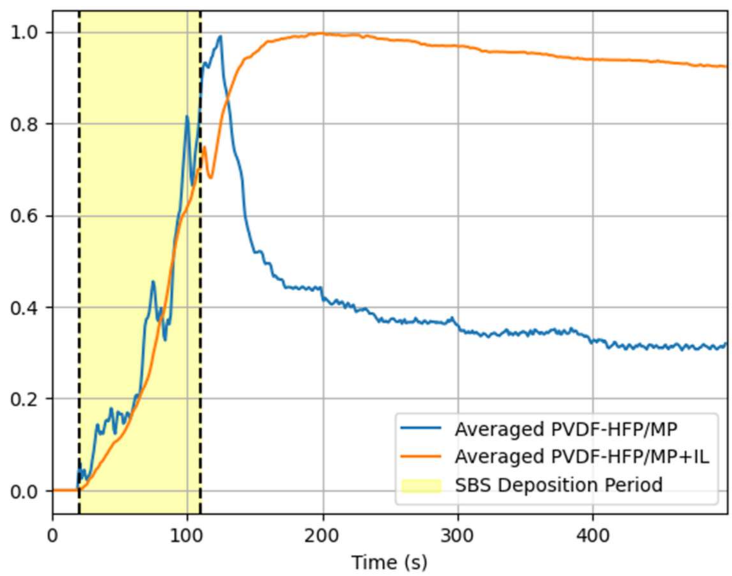

Figure 21. Comparison of post-tensioning profiles for PVDF-HFP/MP nanofibers with and without ionic liquid. The inclusion of ionic liquid results in a sustained high-tension state, whereas fibers without ionic liquid show a rapid decrease in tension post-spinning.

The experimental data captured in the provided graph (Figure 22) clearly demonstrates a significant relationship between the weight of the fibers and the peak force experienced during the post-tensioning tests of PVDF-HFP with ionic liquid. The graph reveals an exponential increase in force as the weight of the fibers increases, which is described by the equation $y=1.7169e^{22.098x}$, where y is the peak force in grams and x is the weight in grams. This correlation, with a high coefficient of determination ($R^2=0.9868$), indicates that heavier fiber samples tend to retain more internal tension.

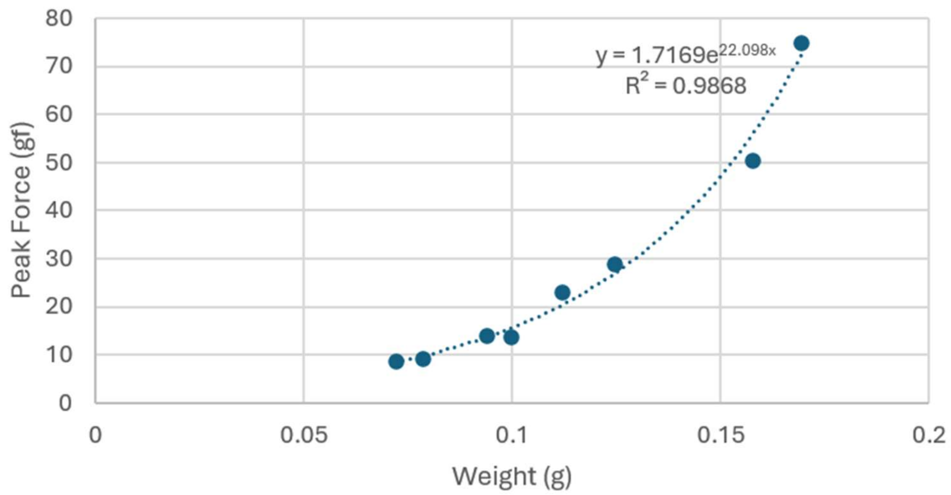

Figure 22. Relationship between fiber weight and peak force during post-tensioning tests of PVDF-HFP with ionic liquid.

3.5 T-Peel Test

The T-Peel tests were designed to measure the amount of force needed to start peeling PVDF-HFP nanofibers off of a PTFE substrate, both with and without an ionic liquid content. PTFE was a distinct benchmark to show the fiber solutions' adhesive properties because of how difficult it is to adhere to its surface. For PVDF-HFP fibers with IL, the force required to initiate peeling was approximately 0.49 N per 5 cm of width, while fibers without IL required a slightly lower force of about 0.44 N per 5 cm of width (Figure 23). This initial peel strength signifies the resistance to separation from the PTFE plate, which is representative of the adhesive bond strength formed by the fibers. During the peel test, no significant visual difference was noted in the peeling behavior between the two sets of fibers.

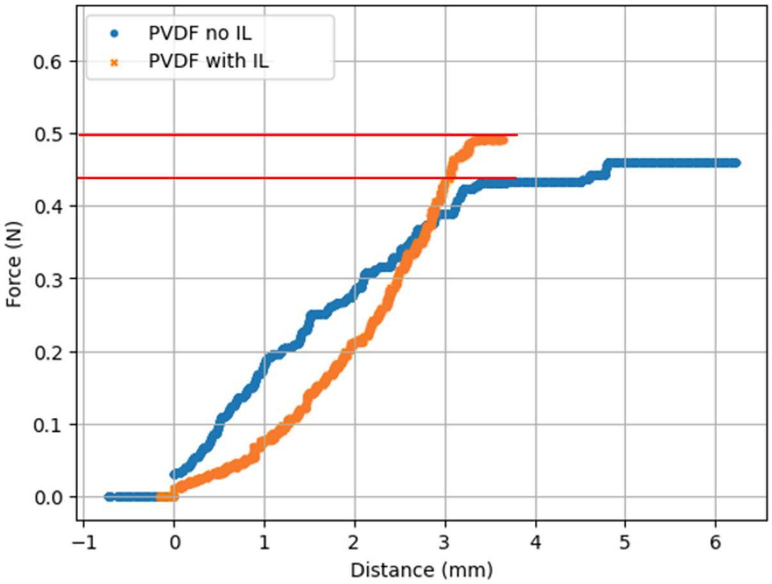

Figure 23. T-Peel test results for PVDF-HFP nanofibers with and without ionic liquid.

Incorporating IL into the PVDF-HFP fibers was primarily to enhance post-tensioning characteristics. This test investigated whether the ionic liquid would negatively impact other physical properties, such as adhesion. The slight difference in the force values between fibers with and without IL suggests that the inclusion of IL did not significantly compromise or affect the adhesive properties of the fibers.

The T-Peel test setup, as applied in our experimental framework, deviates from the conventional industrial standard to accommodate the unique setup of our work. In the industrial setup, both substrates being peeled are typically flexible, and the peel occurs at a consistent 90-degree angle, allowing for a uniform measurement of the peel force over the length of the bond. This consistency produces a graph with a steady force output. In our modified T-Peel test a PTFE base is stationary with only the fiber layer being subjected to the peeling force. This adjustment means that the initial peel occurs at the standard 90 degrees, but as the test progresses, the angle of peel changes as fibers are being peeled off, but the PTFE plate stays stationary, leading to a variable force profile. Therefore, our measurements focus on the force required for the initial separation of the fiber structure from the PTFE, which is a direct measure of the adhesive strength. The resulting graphs from our tests emphasize the peak force at the beginning of peeling, instead of averaged force over length of peeling in classical T-Peel test.

SUMMARY

This work started by addressing the need for more information on using SBS to create unsupported micro/nanofiber architectures. The first study phase showed an immediate need for novel approaches that could be used to fabricate and scale unsupported structures. Progressing from theoretical foundations to practical applications, the study demonstrated the ability to create and subsequently scale up the production of unsupported structures. The development and refinement of the SBS apparatus allowed for experimentation with various polymer solutions to determine the most effective conditions for fiber formation.

Polyethylene oxide (PEO) solutions revealed significant limitations due to their inadequate post-tensioning properties. The PEO fibers were overstretched or failed to maintain structural integrity when subjected to tension. This finding underscored the necessity for exploring alternative materials that could meet the stringent requirements of unsupported structures.

Poly(vinylidene fluoride-co-hexafluoropropylene) showed improved behavior but faced challenges in sustaining post-tensioning without premature breaking. Adding ionic liquids to the PVDF-HFP solution was a breakthrough that significantly improved post-tensioning capabilities and decreased the frequency of material fractures. As shown by the experimental data, the addition of ionic liquids increased mechanical resilience and allowed the fibers to endure higher tensioning forces. These enhancements have promising implications for the future application of SBS fibers, particularly in the construction of complex unsupported structures. The improved properties of PVDF-HFP fibers treated with ionic liquids suggest potential adaptability for specialized uses such as scaffolding in biomedical applications, where dynamic and robust material properties are essential.

This research not only fills a critical gap in the existing scientific literature but also sets a foundational framework for future investigations into scalable production of unsupported, freestanding fiber structures using SBS. The methodologies developed and the insights gained lay a solid groundwork for advancing further optimization of ionic liquid incorporation into SBS process.

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