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ELECTROSPINNING OF UHMWPE NANOFIBERS: CHALLENGES AND SOLUTION STRATEGIES

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Abstract

This study investigates the feasibility of fabricating nanofibers from ultra-high molecular weight polyethylene (UHMWPE) using electrospinning, a technique traditionally limited by UHMWPE's high melt viscosity, poor solubility, and low electrical conductivity. A series of experimental trials were conducted using different polymer grades, solvent systems, conductivity-enhancing additives, and thermal control strategies. Initial trials using decalin revealed homogeneous dissolution at elevated temperatures (~130 °C) but were limited by rapid thermo reversible gelation and high viscosity, which inhibited continuous fiber formation. Thermal stabilization using silicone pad heaters and oil baths extended spinnability, yet precise temperature control remained a challenge. To improve electrospinnability, additives such as tetra-n-butylammonium bromide (TBAB) and cyclohexanone were introduced, resulting in improved conductivity and Taylor cone formation. A novel approach utilizing terpene—a biocompatible and non-carcinogenic solvent—demonstrated promising results in dissolving UHMWPE while reducing toxicological concerns. However, successful and continuous nanofiber production remained constrained by the narrow thermal processing window between the needle tip and collector. The findings highlight the critical interplay between solvent selection, rheology, conductivity, and thermal environment in the electrospinning of UHMWPE.

Keywords: UHMWPE nanofibers; Electrospinning; Green solvent systems; Thermo-reversible gelation; TBAB additive; Terpene

1. INTRODUCTION

Nanofibers have emerged as a transformative class of materials due to their exceptional surface-area-to-volume ratio—approximately 20 times greater than that of meltblown fibers [1], [2]—alongside their superior mechanical responsiveness and functional performance. These characteristics make nanofibrous structures highly desirable for advanced applications in filtration, energy harvesting, medical textiles, and composite reinforcements.

Among the polymers employed for nanofiber fabrication, Ultra-High Molecular Weight Polyethylene (UHMWPE) has achieved significant attention owing to its unique balance of mechanical robustness, lightweight nature, and chemical inertness [3], [4]. As a linear polyolefin with a molecular weight typically ranging from 3.5 to 7.5 million g/mol, according to the American Society of Standards and Testing (ASTM) [5], UHMWPE exhibits exceptional tensile strength (up to 3.5 GPa), low density (~0.93 g/cm³), modulus of elasticity between 0.5–0.8 GPa, and a high melting point (138–142 °C). It also features a broad service temperature range (−169 °C to 90 °C), glass transition around −110 °C, and outstanding resistance to wear, creep, and environmental stress cracking [6]. These remarkable attributes make UHMWPE indispensable in critical applications across various sectors—aerospace (radomes, propeller blades), defense (bulletproof armor, helmets), biomedical (orthopedic implants, surgical sutures), marine (ropes, mooring cables), and renewable energy (wind turbine blades, solar panel mounts) [7], [8].

Despite this impressive properties and broad application landscape, the transformation of UHMWPE into nanofibrous form remains a formidable challenge, primarily due to its ultra-high molecular weight, poor solubility, and extremely high melt viscosity [9], [10]. Several advanced spinning techniques have been investigated for fabricating UHMWPE fibers, each offering partial solutions but accompanied by critical limitations. Gel spinning, a commercially established method, is the most widely used technique for producing UHMWPE filaments on an industrial scale. It involves dissolving UHMWPE in solvents such as decalin to form a concentrated gel, typically in the range of 5–10 wt. % polymer concentration. The gel is then extruded, cooled, and subjected to multi-stage drawing to achieve high molecular chain orientation and crystallinity. This method produces fibers with good mechanical properties, including tensile strengths up to 3.5 GPa and moduli around 120 GPa [4], [10]. However, it also requires complex and energy-intensive post-processing steps, including solvent extraction and multi-stage hot-drawing. However, the fibers produced through gel spinning are typically obtained as individual filaments with diameters in the submicron range and are not structured into fibrous membranes. This structural limitation substantially reduces their specific surface area and thus constrains their suitability for surface-driven applications such as filtration, catalysis, and sensing, where membrane architecture is critical. As a result, gel-spun UHMWPE filaments are primarily employed in ballistic and protective textiles, where high strength and modulus are prioritized over surface functionality [11].

Alternative methods such as solid-state deformation and flash spinning have also been explored for producing UHMWPE fibers. Solid-state deformation involves mechanically stretching UHMWPE in its semi-crystalline state to create highly oriented and crystalline fibers without using solvents [12]. While this method is environmentally favorable, it has major drawbacks, including low productivity, and limited control over fiber diameter and uniformity, especially at large scales [13]. In contrast, flash spinning produces fibrous networks by rapidly evaporating solvent from a polymer solution under high pressure (8–20 MPa) and temperature (150–210 °C) [10]. Although it offers a quick, single-step process, flash spinning struggles with poor fiber alignment, inconsistent morphology, and requires carefully controlled solvent conditions [4], which limits its practical use for nanofiber membrane production.

Electrospinning presents a promising pathway for nanofiber fabrication of fibers typically below 500 nm in diameter with superior surface functionality. There are very few studies on the development of fabrication of UHMWPE nanofibers, as because of the polymer's high melt viscosity, poor solubility in common electrospinning solvents, and low dielectric response impede jet formation and continuous fiber production. To address these issues, researchers have used salt additives (e.g., TBAB) [4], and polymer blending strategies (e.g., with HDPE or PEO) [14]. Some recent studies have shown that the electrospinning of UHMWPE polymer had been achieved by blending them with lower molecular weight polyolefins, such as HDPE. Nayak et al. (2023) [14] demonstrated that electrospun UHMWPE/HDPE blended fibers exhibit smoother surface topography, and better molecular alignment. These findings highlight the critical role of solution composition and structural control in the development of high-quality UHMWPE nanofibers [9], [14], [15]. While these modifications have enabled limited fiber formation, most reported processes remain confined to laboratory-scale demonstrations and lack the reliability, consistency, and throughput required for industrial viability.

In the present work, we conduct a systematic investigation into electrospinning strategies for UHMWPE nanofiber fabrication, with the objective of developing a reproducible and scalable process suitable for industrial applications. Building on prior research, the study examines the synergistic effects of polymer blending, solvent selection, and process parameter optimization. Special emphasis is placed on solution rheology, polymer–solvent interactions, and additive use to overcome the inherent processing challenges of UHMWPE and achieve consistent fiber morphology and mechanical performance.

EXPERIMENTAL SECTION

MATERIAL USED

Two grades of ultra-high molecular weight polyethylene (UHMWPE) were used as the primary polymer: one with a molecular weight (Mw) of approximately 5 million g/mol and another of 3.3 million g/mol. Both were procured in powdered form from Sigma-Aldrich (USA) and used as received. The solvents used included decahydronaphthalene (decalin, 98% purity, TCI Chemicals Pvt. Ltd., India), terepene oil, tetra-n-butyl ammonium bromide (t-BAB), and cyclohexanone (CH). Terepene oil was procured from local industrial sources. Cyclohexanone was also obtained from TCI Chemicals Pvt. Ltd., India. All solvents were of reagent grade and employed without additional purification.

To modify solution behavior and enhance electrospinnability, the following additives were utilized: tetra-n-butyl ammonium bromide (t-BAB) (to improve solution conductivity), and cyclohexanone (as a polar co-solvent). No drying, filtration, or other pre-treatment steps were applied prior to usage.

EXPERIMENTAL APPROACHES FOR UHMWPE NANOFIBER FORMATION

Approach I: UHMWPE Solution-Based Electrospinning

This approach explored the feasibility of fabricating UHMWPE nanofibers via electrospinning using decalin as the primary solvent (as shown in the Figure 1). Two grades of UHMWPE—Mw = 5 × 10^6 g/mol and Mw = 3.3 × 10^6 g/mol—were tested, each at a polymer concentration of 0.5 wt. %. In both cases, magnetic stirring at ambient conditions led to polymer swelling without complete dissolution, resulting in inhomogeneous dispersions (Figure 2a). Upon heating the mixtures to 130 ± 5 °C, below the boiling point of decalin (186 °C), visually homogeneous solutions were obtained (Figure 2b). However, a marked difference in solution behavior was observed: the high molecular weight sample (Mw = 5 × 10^6 g/mol) exhibited very high viscosity, whereas the lower molecular weight sample (Mw = 3.3 × 10^6 g/mol) produced a comparatively less viscous solution, reflecting the impact of polymer chain length on rheological properties. Importantly, a less viscous solution is more favorable for electrospinning, as it facilitates stable jet formation and elongation. Despite improvements in homogeneity, both solutions underwent thermo-reversible gelation, rapidly solidifying upon cooling to room temperature (~25 °C) (Figure 2c). Consequently, no fiber formation was achieved in these initial trials due to insufficient jet elongation and blockage caused by premature gelation at the syringe needle.

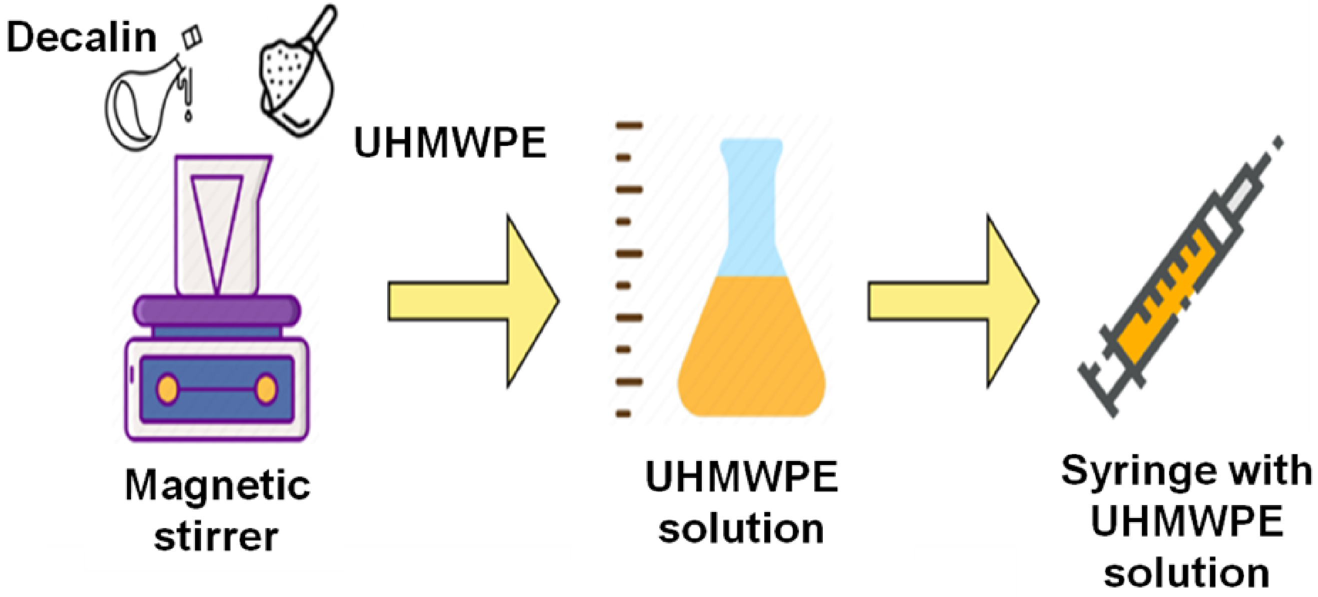

Figure 1: Solution preparation of the UHMWPE polymer and decalin as a solvent

In an effort to address this limitation, Trial 3 introduced thermal and airflow modifications to the electrospinning setup using the Mw = 3.3 × 10^6 g/mol solution, selected for its comparatively favorable viscosity. A silicone pad heater was applied to the glass syringe barrel to maintain solution temperature and prevent early gelation (as shown in the figure 3), while a blower was directed at the needle tip to reduce solid buildup. Electrospinning was conducted under the parameters listed in Table 1, including a flow rate of 1 ml/h, tip-to-collector distance of 10 cm, applied voltage of 10 kV, and collector drum speed of 450 rpm. Under these conditions, the formation of a stable Taylor cone confirmed successful jet initiation. However, solidification at the needle tip ultimately led to flow obstruction, preventing continuous fiber formation. This trial demonstrated that while external thermal support can temporarily extend the solution's spinnability window, long-term electrospinning remains constrained by the intrinsic thermo-gelation behavior of the UHMWPE–decalin system.

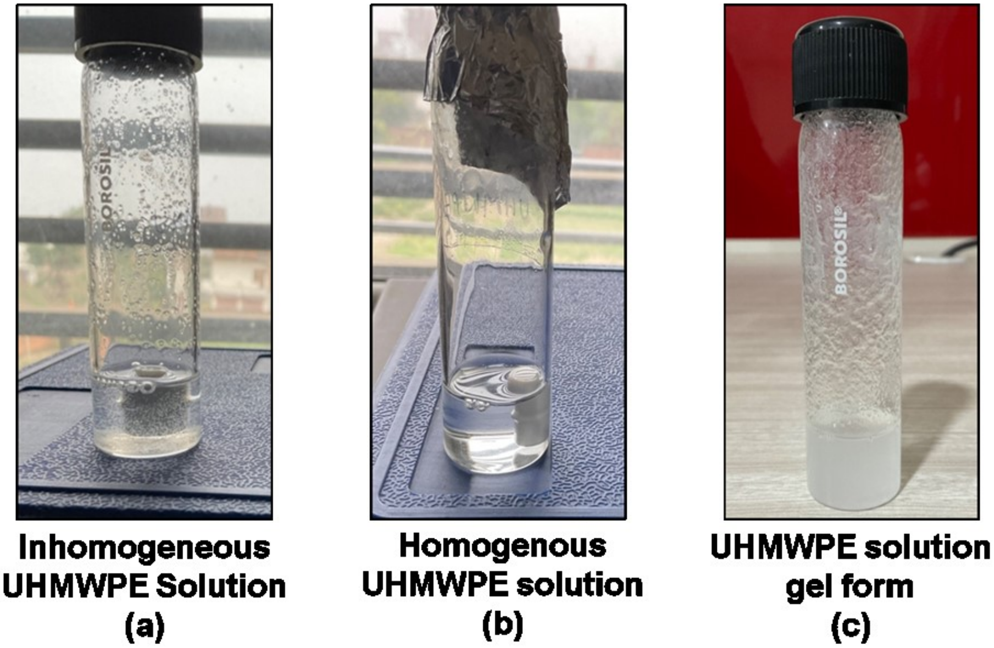

Figure 2: Visual progression of UHMWPE solution in decalin during the dissolution process. (a) Initial condition (at room temperature) showing partial dispersion of UHMWPE polymer. (b) Homogenous UHMWPE solution (immediately after removal from the oven at 130°C). (c) Gel form of the UHMWPE solution (after sometime placing at room temperature)

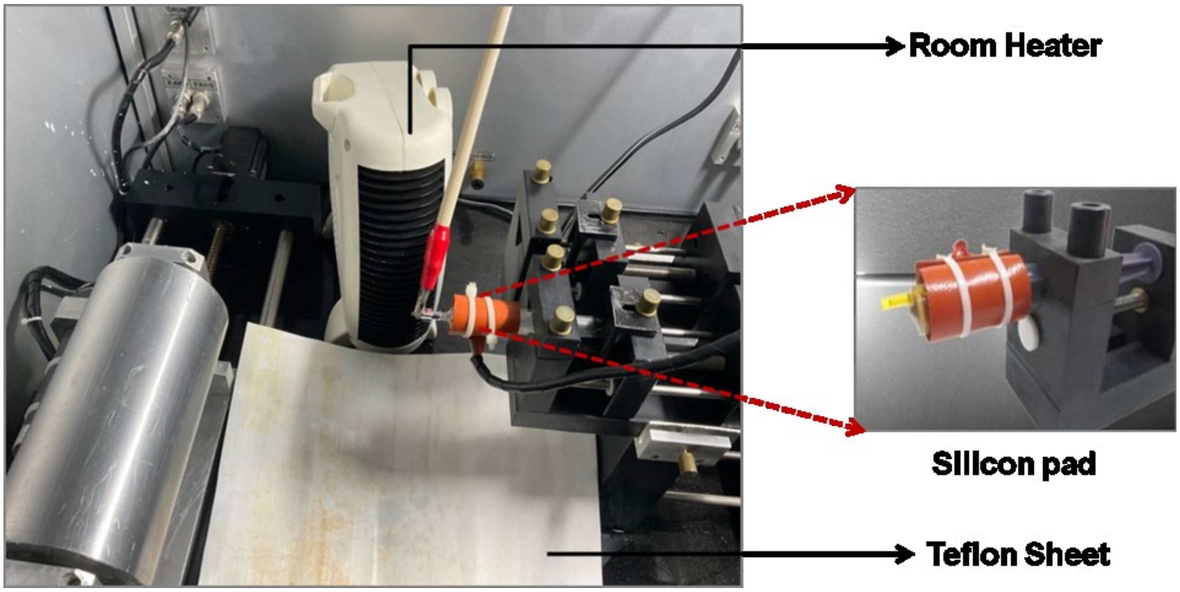

Figure 3: Experimental setup for electrospinning through silicone pad

In Trial 4, further modifications were made to address the persistent issue of solution solidification at the needle tip and to enhance the electrical conductivity of the system. UHMWPE with Mw = 3.3 × 10^6 g/mol was used at a concentration of 0.5 wt. % in decalin. In this setup, the needle was removed, and aluminum foil was wrapped around the tip of the syringe, onto which the high-voltage cable was directly connected. Despite this modification, the polymer solution again solidified at the tip, halting fiber formation. Notably, low solution conductivity was identified as a major limiting factor, impeding stable electrospinning. These observations suggest that the electro-hydrodynamic force was insufficient to sustain continuous jet formation. It was concluded that the addition of conductivity-enhancing additives or ionic fillers would be necessary in future trials to overcome this challenge and facilitate uninterrupted fiber spinning.

Table 1: Electrospinning Process Parameters Used in the Experiment

Parameters	Values
Solvent (Boiling Temperature)	Decalin (186°C)
Solution Concentration	0.5% by wt.
Flowrate	1 ml/hr
Distance between collector and needle tip	10 cm
Voltage	18 KV

Approach II: Heated Oil Bath-Assisted Electrospinning

In this approach, a silicone oil bath was employed to thermally regulate the UHMWPE solution during electrospinning (as shown in the Figure 4). A UHMWPE sample with Mw = 3.3×10^6 g/mol was dissolved in decalin (0.5 wt. %), and the glass syringe was fully immersed in the oil bath, leaving only the needle tip exposed. The bath was intended to maintain the solution temperature at 130 ± 5 °C, significantly below the boiling point of decalin (186 °C), to prevent premature gelation and ensure sufficient molecular mobility for fiber formation.

Under these conditions, initial fiber formation was observed, confirming the partial viability of the method. However, it proved extremely difficult to maintain the oil bath temperature consistently close to 130 °C. This was due to the narrow thermal window between the UHMWPE dissolution point and its melting temperature, which led to partial melting of the polymer when the bath temperature slightly exceeded the target. As a result, molecular chain alignment and crystallization—both essential for stable nanofiber formation—were compromised. Furthermore, the solution exhibited very low electrical conductivity, and even at an applied voltage of 25 kV, the Taylor cone remained unstable, preventing continuous electrospinning.

This trial demonstrated that while thermal insulation using an oil bath can delay solidification, precise temperature control is critical, and the system's low conductivity remains a fundamental limitation. There is a need to incorporate the conductivity by addition of the additives alongside improved thermal management strategies to establish a stable electrospinning process for UHMWPE–decalin systems.

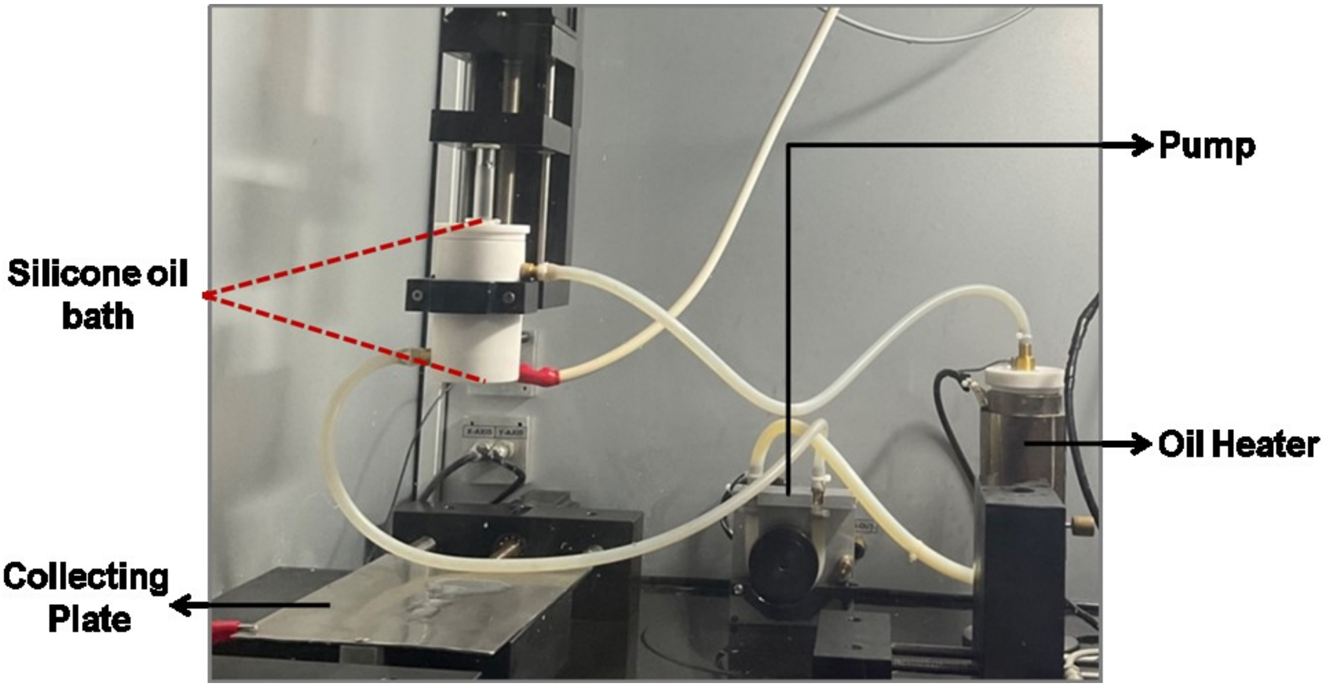

Figure 4: Experimental setup for electrospinning through silicone oil bath

Approach III: Terpene-Based Electrospinning with Additive-Enhanced Conductivity

Terpene—a non carcinogenic, biologically safe solvent—was evaluated as a sustainable alternative for dissolving UHMWPE. A 0.5 wt % solution of UHMWPE (Mw = 3.3 × 10^6 g/mol) was obtained by heating to 130 ± 5 °C, yielding a clear, homogeneous solution; to the authors' knowledge, terpene has not previously been reported for UHMWPE dissolution. On cooling to ambient temperature the solution exhibited thermo reversible gelation, analogous to behavior observed in decalin based trials.

To overcome the intrinsically low conductivity of terpene, tetrabutyl¬ammonium bromide (TBAB) and a small aliquot of cyclohexanone (CH) were incorporated directly into the terpene phase, in 1:1 ratio. The additives improved charge transport sufficiently for stable Taylor cone formation at low applied voltage (~10 kV).

Continuous fibre production was nevertheless impeded by the thermal processing between the heated needle (~130 °C) and the collector surface (~25 °C). Minor temperature excursions produced either (i) premature gelation at the needle tip, blocking flow, or (ii) solidification of the jet prior to deposition, both of which interrupted spinning. Hence, although a terpene/TBAB/CH medium minimizes toxicological concerns and supports initial jet formation, rigorous thermal control throughout the spinning zone remains essential for sustained, large-scale UHMWPE nanofiber manufacture.

Table 2: Summary of electrospinning approaches and experimental trials for UHMWPE nanofiber fabrication

Approach	Trial	Polymer (M_w & wt. %)	Solvent System	Additive	Key Observations	Outcome
I Approach Solution-Based Electrospinning	Trial 1	5×10^6 g/mol 0.5 wt.%	Decalin	None	High viscosity, gelled on cooling	No fiber
	Trial 2	3.3×10^6 g/mol 0.5 wt.%	Decalin	None	Lower viscosity, but thermo-reversible gelation	No fiber
	Trial 3	3.3 × 10^6 g/mol 0.5 wt.%	Decalin	None	Stable Taylor cone, solidification at tip	No continuous fiber
	Trial 4	3.3 × 10^6 g/mol 0.5 wt.%	Decalin	None	Solidification at tip, low conductivity	No fiber
II Approach Heated Oil Bath Electrospinning	Trial 5	3.3 × 10^6 g/mol 0.5 wt.%	Decalin	None	Initial spinning started, but melting occurred due to poor temp control	No continuous fiber
III Approach Terpene-Based Green Electrospinning	Trial 6	3.3 × 10^6 g/mol 0.5 wt.%	Terpene	None	Clear solution, reversible gelation on cooling	No trial performed
	Trial 7	3.3 × 10^6 g/mol 0.5 wt.%	Terpene oil	TBAB + CH	Improved conductivity, unstable thermal zone	Initial fiber observed, no continuity

CONCLUSION AND FUTURE SCOPE

This study presented a systematic investigation into the fabrication of nanofibers from ultra-high molecular weight polyethylene (UHMWPE) via electrospinning, employing various solvent systems, polymer molecular weights, and processing strategies as shown in Table 2. Initial trials using decalin revealed that although UHMWPE could be dissolved at elevated temperatures (~130 °C), the solutions were highly viscous and exhibited strong thermo reversible gelation, which inhibited stable jet formation and continuous fiber production. Thermal regulation through silicone pad heating and oil bath immersion temporarily extended spinnability but lacked the precision needed to maintain consistent fiber formation. Additionally, the inherently low conductivity of UHMWPE–solvent systems was found to be a major limiting factor.

To address these challenges, conductivity-enhancing additives such as tetrabutylammonium bromide (TBAB) and cyclohexanone were introduced. These additives improved charge transport, enabling Taylor cone formation under moderate voltages, although temperature instability still disrupted continuous spinning. A promising alternative solvent, terpene, was successfully used to dissolve UHMWPE and demonstrated improved safety and biocompatibility. When combined with co-solvents and additives, terpene-based solutions supported initial fiber formation, but the narrow thermal processing window remained a significant bottleneck.

Future work should prioritize the development of advanced thermal management strategies. Specifically, the integration of an infrared heater directly at the nozzle tip is recommended to initiate controlled gel formation and stabilize the extrusion interface. Additionally, the electrospinning chamber should be thermally engineered to ensure a gradual and controlled temperature transition from ~130 °C at the needle tip to ambient conditions at the collector, rather than a sudden drop to room temperature (~25 °C). These improvements will be critical to achieving continuous, scalable, and reproducible nanofiber production from UHMWPE systems.

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