

A concise overview of the aramid fiber spinning process

Yogesh Hande

The Bombay Textile Research Association, LBS Marg, Ghatkopar (W), Mumbai 40086, India.

Abstract

The article covers Aramid fibers (AFs), renowned for their exceptional strength, heat resistance, and versatility, which have a rich history that encompasses groundbreaking discoveries and technological advancements. The inception of lyotropic liquid crystals was a pivotal moment, providing a foundation for the development of lyotropic solutions specific to AFs. These solutions, derived by dissolving high molecular weight aramids in suitable solvents, play a crucial role in the synthesis of these advanced fibers. Two prominent synthesis methods involve the solution polymerization of aromatic diamines and aromatic dicarboxylic acid chlorides. AFs, post-synthesis, undergo various spinning techniques, including Dry spinning, Wet spinning, Dry-jet wet spinning and Electro spinning, each contributing distinct characteristics to the final product. The applications of AFs span a broad spectrum, encompassing protective clothing, industrial materials, aerospace components, and military applications. As we delve into the intricacies of AFs spinning, it is imperative to consider the future outlook, anticipating further advancements in synthesis methods, spinning techniques, and innovative applications that will contribute to the continued evolution of this remarkable class of fibers in materials science.

Keywords:

Lyotropic liquid crystal, Spinning, Polymerisation

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1.0 Introduction

Aramid fibers (AFs) are a class of high-performance organic polymer fibers known for their outstanding mechanical properties, heat resistance, and chemical stability. Since their invention in 1964, AFs have become indispensable materials across a wide range of applications from aerospace and defence to sports equipment and electrical insulation. [1–5] The unique properties of aramids are attributed to their molecular structure consisting of aromatic rings linked by amide groups. The high degree of molecular orientation achieved during the spinning process also imparts strength and stiffness along the fiber axis. Commercial AFs are predominantly based on two polymers – poly (p-phenylene terephthalamide) (PPTA) marketed as Kevlar and Twaron, and poly (m-phenylene isophthalamide) (MPIA) known commercially as Nomex. Recent years have also seen the emergence of other speciality aramids such as poly (p-phenylene benzobisoxazole) (PBO) and heterocyclic aramids with enhanced thermal and chemical resistances [6–9]. A range of dry and wet spinning techniques have been employed over the decades to produce commercial AFs. The choice of spinning process depends on the polymer type, desired fiber properties and process economics. An overview of the different spinning methods along with key developments in aramid spinning technology is provided in this review. More recently, the fabrication of aramid

nanofibers has also garnered attention given their potential to achieve superior mechanical performance and multifunctionality compared to conventional aramids. Current research trends in this emerging area are examined.[10] Overall, this review provides a comprehensive outlook on the different spinning methods employed for manufacturing AFs along with key milestones in process development over past decades. Advances in the spinning of aramids for tailored applications as well as early efforts on novel AFs have also been discussed. The challenges and opportunities for future innovation are highlighted.

2. Development History of Aramid Fibres

In the 1960s, the development of AFs, driven by the need for heat-resistant and strong materials, marked a significant milestone. DuPont led the way by introducing Nomex, a meta-aramid fiber, in 1967, followed by the higher-performing para-aramid fiber, Kevlar, in 1971. Kevlar quickly found applications in diverse fields such as protective gear, tyres, ropes, and composites. Despite early research by Soviet scientists on high-strength heteroaromatic fibers like SVM in the 1970s, challenges in the spinning process and mechanical properties hindered commercialization compared to Kevlar. In the 1980s, Russia overcame these challenges and introduced the para-aramid Terlon. Other major producers, Teijin and AkzoNobel, later

*Corresponding author,

E-mail: uhmwpe.btra@gmail.com

introduced meta- and para-aramid fibers, namely Technora and Twaron. The 1990s saw the introduction of high-temperature-resistant poly (p-phenylene benzobisoxazole) (PBO) fibers as advanced 'super fibers.' Recently, South Korean and Chinese companies have actively developed domestic production capabilities for both commodity and speciality aramids. Over the past five decades, continuous refinement of manufacturing processes has improved uniformity, tensile strength, modulus, and other properties of AFs, meeting diverse application needs. Aramid spinning technologies have evolved, enabling rapid scale-up from lab-based research to high-volume industrial production. Advances in AFs technology have significantly enhanced the strength of AFs fibrous products, making them crucial for cutting-edge applications. The global manufacturing engagement in AFs and related composites reflects their increasing demand across sectors like ballistic protection, energy, equipment manufacturing, and intelligent wearables. The growing number of annual publications and citations related to AFs underscores the ongoing advancements and widespread applications of these materials over the past few decades. [11]

Table1. The history of commercial AFs [6]

Year of Invention	Name of Invention
1967	Dupont Nomex
1970	Armos and Dupont Kevlar
1972	SVM (superhigh-strength and high-modulus)
1978	Teijin Conex
1985	Teijin Technora
1986	Terlon
1990	Nobel Twaron
1995	Rusar
2004	PBO Fiber
2006	Tayho Tametar
2009	Kolon Heracron
2011	Hyosung Alkex
2018	Tayho Tapanan

3. Invention of lyotropic liquid crystals

In a solution, a flexible polymer chain assumes a random coil shape as shown in Figure 1 (a), while rigid chains, composed of stiff units, display a rodlike structure as shown in Figure 2 (b). As the concentration of rigid molecular chain polymers increases, molecular chains densely pack together as shown in Figure 1 (c). Flory's equation[12] predicts the transition

from an isotropic to an anisotropic phase beyond the critical concentration ψ^* , where ψ^* decreases with a higher axial ratio (x) or molecular rigidity.[13].

$$\psi^* = \frac{1}{8} \left(1 - \frac{2}{x}\right) \dots (1)[14]$$

Hence, polymers with a high axial ratio, particularly those rigid or stiff, are preferred for creating anisotropic solutions. These solutions form liquid crystals with domains where molecules align uniformly (director), facilitating extended molecular chain structures as shown in Figure 1(d)[12]. Viscosity generally increases significantly below the critical concentration as shown in Figure 2[15]

A notable exception, discovered by Kwolek, defied this trend. Above the critical concentration, p-aramid solutions exhibited opacity, and viscosity sharply decreased. This breakthrough led to the development of high-modulus, high-strength fibers, exemplified by the commercially successful Kevlar® (Fiber B) in 1971, surpassing traditional fibers like polyester tyre yarn in tensile strength and modulus. Before DuPont's p-aramid, Monsanto had introduced X-500[16], a polyamide-hydrazide. Post-Kevlar's success, researchers explored various aramids, developing solvent-free liquid crystalline polyacrylates to eliminate costly solution processing. Notably, these new stiff polymers predominantly feature a linear backbone.

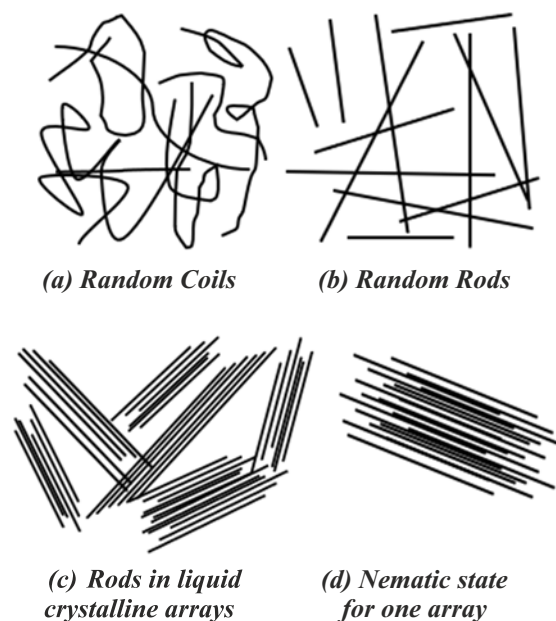


Figure 1. Schematic representation of polymer state in solution

characteristic of classified super fibers. Nomex® has found extensive use in thermal and electrical insulation applications. As a distinctly rigid para-version of aramid, Kwolek4 synthesized poly(p-benzamide) (PBA) and poly (p-phenylene terephthalamide) (PPTA), both capable of forming liquid crystalline solutions. Consequently, the p-aramid fiber Kevlar® was developed and brought to market in 1971, also by DuPont Company.

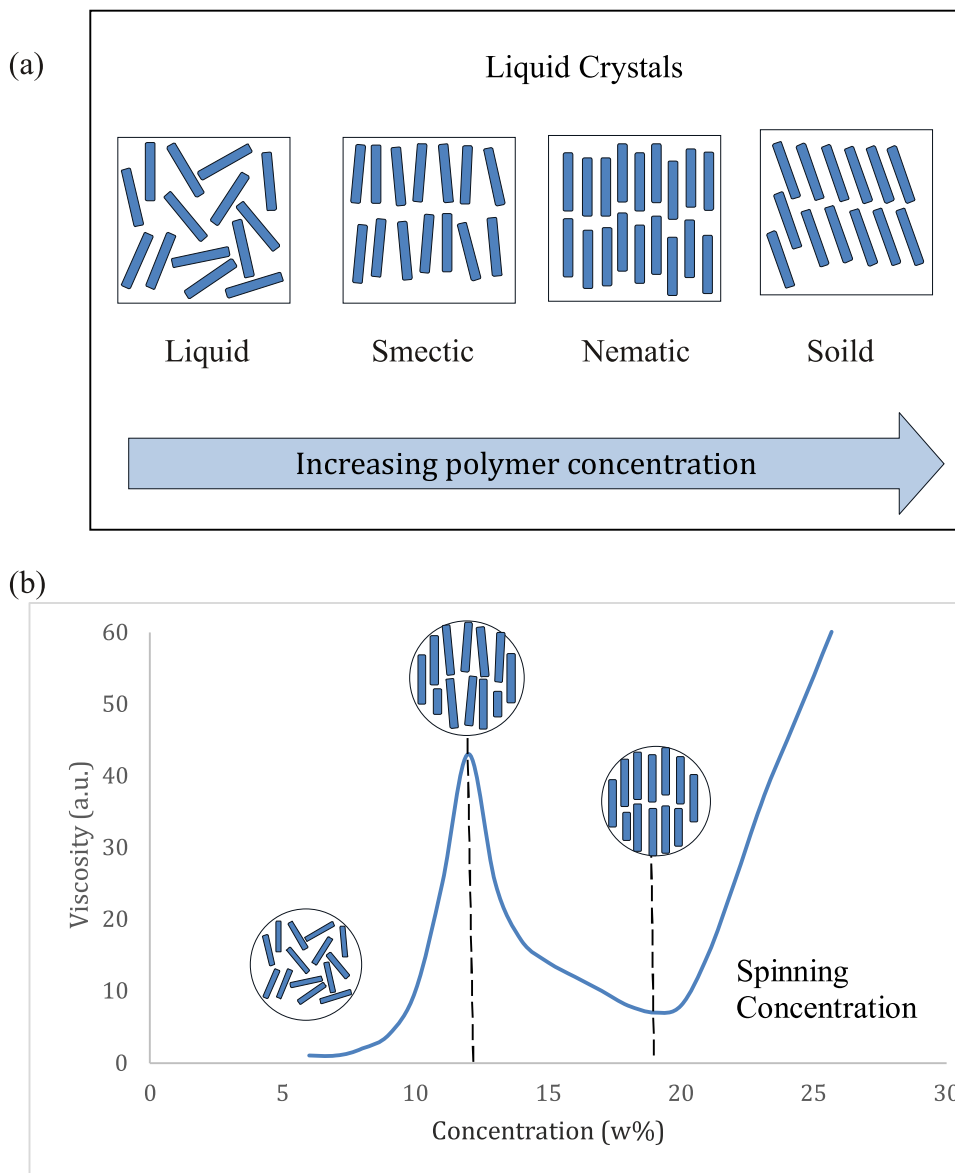


Figure 2. (a) Structure of lyotropic nematic phase concerning concentration. (b) A typical viscosity vs. concentration curve for lyotropic solutions [17]

4. Aramid solution

Aramid polymers possess a high melting point, often surpassing their decomposition temperature. This characteristic renders the melt spinning of aramids impractical. Consequently, aramid fibers are manufactured through solution spinning. However, dissolving aramids poses a challenge due to their rigid structure. Typically, highly polar solvents, either with or without inorganic salts or strong acids, are employed for dissolution. Homopolymers like poly (m-phenylene isophthalamide) (m-DPI) can produce isotropic solutions in solvents such as N-methyl-2-pyrrolidone (NMP) and DMAc. In the case of p-aramids, solubility can be enhanced through copolymerization, as discussed earlier. Notably, p-aramids form isotropic solutions only at low polymer concentrations. For instance, poly (p-phenylene terephthalamide) (PPTA)

achieves isotropic solutions at concentrations below 10 wt% and ambient temperature[1].

Semirigid polymers exhibit molecular orientation under external forces like electrical, magnetic, shear, and elongational flow. This behaviour is evident in lyotropic solutions, such as poly(p-benzamide) and PPTA. The molecular orientation of rod-like molecules of PPTA along the axis, with the degree of orientation denoted by β ranging from 9° to 12° . Factors like solution concentration, solvent, the molecular weight of the polymer, and temperature influence orientation and phase behaviour in lyotropic nematic polymer solutions. In the case of PPTA in 100% sulfuric acid, viscosity and molecular arrangement are concentration-dependent, forming smectic and nematic phases in liquid crystals[1].

Depicts the viscosity and molecular arrangement changes with concentration. At lower concentrations, viscosity initially increases with little or no crystal domain orientation. However, at higher concentrations (18–23% PPTA), viscosity decreases as crystal domains perfectly orient, exhibiting anisotropic behaviour. This concentration range, with low viscosity and highly oriented polymer, is crucial for spinning. In contrast to isotropic polymers, where increased viscosity is expected with concentration, lyotropic solutions show decreased viscosity due to the formation of the nematic liquid crystal phase[1].

For solution spinning, low viscosity at high polymer concentration is essential. A phase diagram for PPTA in 100% sulfuric acid, where the critical concentration depends on molecular weight and temperature. Dopes at concentrations of 18–23% are solid up to about 80°C, necessitating melting before spinning. Conversely, for coagulation at low temperatures, dry-jet-wet spinning is employed. In this process, the spinning of PPTA in the nematic phase leads to fiber precipitation in the air gap, with acid removal occurring in the coagulation bath. The phase diagram indicates that dopes up to 10% concentration have low viscosity and can be wet-spun[17].

5. Synthesis of Aramid fibres

Afs are typically synthesized through polycondensation reactions between aromatic diamines and aromatic diacyl chlorides rather than aromatic dicarboxylic acids due to challenges with the chemical reactivity of the latter. The reactions involve amine groups (-NH₂) condensing with acyl chloride groups (-COCl) to form amide bonds (-NH-CO-) and hydrogen chloride (HCl) as a byproduct. Over the past five decades, researchers have developed various synthesis routes for aramids including interfacial polycondensation, low-temperature direct polymerization, ring-opening polymerization, non-aqueous suspension polymerization, and reactions in microchannel reactors. This section reviews some of the key polymerization methods, their reaction mechanisms, the monomers used, as well as merits and limitations of each technique for manufacturing commercial aramid fibers.

5.1 Interfacial Polycondensation

DuPont pioneered interfacial polycondensation for synthesizing aramids in the 1950s [17]. This involves dissolving aromatic diamines such as p-phenylenediamine (PPD) or m-phenylenediamine (MPD) in water with minor amounts of NaOH or Na₂CO₃. Aromatic diacid chlorides like terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC) are dissolved in an organic solvent immiscible with water such as benzene or carbon tetrachloride. When the diacid chloride solution is added to the aqueous diamine under stirring, a polycondensation reaction occurs at the liquid-liquid interface resulting in the formation of aramid polymer films [17-18]. While providing an intuitive route for para-aramid synthesis, a limitation is that reactions are conducted near room temperature. However, the heat released leads to temperatures rising to 50-60°C during polymerization which reduces process control and efficiency [20]. Hence optimizing the polymerization process for rapid and consistent aramid fiber production remains an area requiring further improvement.

5.2 Low-Temperature polycondensation

As an alternative method, low-temperature polycondensation was developed by DuPont during the 1960s to overcome the temperature increase described above during the interfacial polycondensation process. Both m-aramid and p-aramid can be prepared using this method. depicts their reaction mechanisms, respectively. This methodology uses various chemicals such as N-methyl pyrrolidone (NMP), N, N-dimethylacetamide (DMAc), and hexamethyl phosphoric triamide (HMPA; it is being phased out owing to its carcinogenicity and difficult recyclability). Typically, the synthetic process starts with the complete dissolution of PPD, anhydrous LiCl/CaCl₂, and pyridine in the selected solvent. The mixture is then cooled to 258 K (-15.15°C) in an N₂ atmosphere before being stirred vigorously. An equal molar amount of TPC is added. As the reaction progresses, a viscous paste-like gel product is produced. After stirring, the reaction mixture is permitted to stand overnight before being heated to room temperature. Finally, the obtained mixture is washed with deionized water to remove any remaining solvent and HCl [20-21]. The

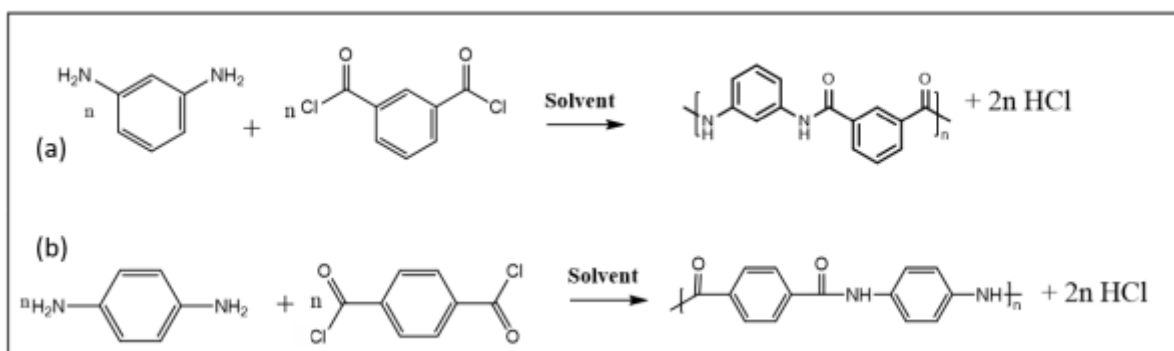


Figure 3. Synthesis mechanism of the (a) m-aramid, (b) p-aramid [17]

synthesis method for m-aramid is similar to that for p-aramid. the reaction mechanism for producing PBO. Specifically, this process includes the addition of equal molar amounts of 1,4-diamino resorcinol dihydrochloride and TPC and a certain amount of phosphoric acid in a container with N₂ gas, stirring, and dehydrogenation at 65°C and 80°C for a certain period before being cooled to room temperature. Then, P₂O₅ is added to achieve a concentration of 75–80% and generate poly (phosphoric acid). Subsequently, the mixture is stirred at 80°C for 2 hrs and cooled to room temperature. Then, P₂O₅ is added again to increase the concentration to 83%. The stirring process is maintained while the temperature is increased at predetermined intervals (16 hrs at 160°C and 4 hrs at 190°C). Finally, the product is washed with water and dried to obtain PBO. Currently, this method is efficient for commercially synthesizing AFs [22–24].

5.3 Direct polymerisation

Polymerization, a widely adopted method in industrial production [25-26], offers benefits such as simplicity, rapid reactions, and cost-effectiveness. Direct polymerization facilitates diverse AFs production by combining various raw chemicals. Teijin employs this technique for Technora[28] synthesis, involving the polycondensation of 3,4'-diaminodiphenyl ether (3,4'DAPE), PPD, and TPC, eliminating inorganic salt co-solvents like LiCl or CaCl₂ to cut production costs. However, challenges like exothermic reactions and toxic solvents like HMPA and NMP pose environmental concerns. Yotsumoro and Shin [6] proposed similar methods for PPAT synthesis, using sulfobenzides for successful PPTA synthesis. Ongoing research explores novel synthetic methodologies, but industry acceptance is hindered by cost and controllability issues. Yamazaki et al. achieved high molecular weight poly-p-benzamide through direct polycondensation in NMP-pyridine solutions with LiCl and CaCl₂[28–30]. Higashi et al. synthesized polyamides using triphenyl phosphite in a direct polycondensation reaction with LiCl. Silver's [32] direct polycondensation method for p-aramid using SO₃ faces challenges like sulfonation. Shoji [33] proposed synthesizing aramids by polymerizing aromatic dicarboxylic acids with ether-linked aromatic diamines, producing AFs with enhanced chain mobility, lower T_g, and suitable melting points. While these strategies laid the groundwork for industrial AF production, direct polymerization has waned due to high raw material costs, reaction conditions, and secondary reactions.

5.4 Ring-opening Polymerization

Metal-based catalysts play a crucial role in ring-opening polymerization by offering high activity and precise control over polymer characteristics such as dispersion, microstructure, and regularity[33-34]. Numerous studies have focused on palladium catalysts for the synthesis of AFs. Yoneyama[36] developed a technique using a palladium catalyst for the carbonylation polymerization of aromatic

dibromides and diamines with carbon monoxide (CO), leading to the synthesis of AFs. Perry[37] optimized this procedure by synthesizing aramids without CO, emphasizing the importance of a marginal excess of diamine monomers and a high final molecular weight of m-diiodo benzene monomers. This method is considered an attractive alternative for producing high-molecular-weight aromatic polyamides due to the remarkable properties of the obtained samples.

Ionic liquids, known for unique properties like nonvolatility, good solubility, and strong electrical conductivity, have advantages such as stable chemical properties, negligible vapour pressure, adjustable acidity, and recoverability. Scientists are exploring their use in synthesizing polyamides, particularly poly (p-phenylene terephthalamide) (PPTA). However, limited information exists on the synthesis of PPTA in pure ionic liquids [37–39], and their use as a polymerization medium tends to yield low-molecular-mass PPTA. Dewilde et al. [41], [42] improved this approach, substituting the NMP/CaCl₂ solution with 3-methyl-1-octylimidazolium chloride as the solvent for PPTA synthesis. The polycondensation reactions in ionic liquids led to the highest recorded molecular weight of PPTA, making them effective media for manufacturing polymers with significant macromolecular masses.

5.5 Non-aqueous Suspension Polymerization

The non-aqueous suspension polymerization technique utilizes a nonreactive solvent to envelop the reactants within the system, preventing their contact with water and oxygen in the air. This creates an advantageous environment for polycondensation reactions[42]. Wang introduced a method for producing PPTA through non-aqueous suspension polycondensation. In this setup, the dispersed phase comprised a solution of NMP-CaCl₂, formed by dissolving CaCl₂, PPD, and pyridine in dried NMP, while inert liquid paraffin acted as the continuous phase. The reaction was initiated with the addition of TPC to the non-aqueous suspension, and after a specific duration, the reaction was quenched by flushing the system with deionized water. Compared to the traditional solution polycondensation approach, this non-aqueous suspension polycondensation method offers notable advantages. These include a tightly sealed reaction environment that effectively isolates reactants from oxygen and water, easy elimination of HCl to facilitate the reaction, precise temperature control, and low viscosity, leading to reduced energy costs. However, it is observed that the viscosity of the product increases in the later stages of the reaction, posing challenges to effective stirring. Improvements are needed to enhance product quality further.

5.6 Microchannel Reactors

A microchannel reactor, operating as a continuous-flow reactor with internal dimensions ranging from millimetres to micrometres, offers precise feed control and a high specific

surface area. These features enable rapid material mixing and efficient heat dissipation during reactions[44]. Microchannel reactors find extensive use in various applications such as microwave-enhanced reactions[45], nanoparticle preparation[45-46], biomedical synthesis[48], and green organic catalysis[49]. In recent years, the adoption of microchannel reactor technology for continuous production has become widespread in organic synthesis and polymerization[49-50]. In the context of polycondensation, the microchannel reactor's rapid heat dissipation effectively prevents the broad molecular weight distribution of PPTA induced by temperature increases.

Wang et al.[52] introduced an innovative micro-structured chemical system for synthesizing PPTA polymers. NMP served as the solvent, and anhydrous CaCl₂ acted as the co-solvent. PPD and TPC were dissolved in an NMP/CaCl₂ mixture as precursors. The forward reaction was facilitated by introducing N₂ into the system to eliminate the HCl produced during the reaction. The PPTA prepolymer underwent rapid reaction in the microchannel reactor after the reaction solution was mixed in a micro sieve mixer through the feeding pipeline. Through adjustments in synthesis conditions, a polymer with a weight-average molecular range of 4000–16,000 was achieved. This inventive procedure enhances the safety and convenience of polycondensation processes. However, microchannel reactors do have limitations, including a positive correlation between the viscosity of the reaction mixture and the chain length of the polymer. This phenomenon leads to increased flow resistance, impeding the synthesis of polymers.

6. Types of Spinning of AF

Aramids undergo decomposition either before or during the melting process, necessitating their spinning from a solution. While both dry and wet spinning techniques are applicable, the resulting properties differ based on the polymer structure and the chosen method. The spinning of AFs can be done using dry spinning, wet spinning, dry-jet-wet spinning or electrospinning processes.

6.1 Dry Spinning

After introducing an organic solvent, specifically N-methyl-2-pyrrolidone (NMP) with 3 wt.% CaCl₂, into a reactor under a nitrogen atmosphere, a mixed solution was prepared by adding 50 mol% p-phenylenediamine and 50 mol% cyano-p-phenylenediamine to the reactor, dissolved in the solvent. Following this, 100 mol% terephthaloyl dichloride was introduced to form a polymeric solution containing an aramid polymer. CaO, an alkaline compound, was added to the solution to neutralize hydrochloric acid produced during polymerization, and a vacuum was applied to remove the generated water. The polymeric solution, now containing aramid polymer, underwent heating, and the amount of organic solvent was adjusted to achieve an aramid polymer concentration of approximately 16 wt.%. Subsequently, the polymeric solution was spun through a spinneret into a

fibrous form. The spun fiber passed through nitrogen gas as an inert gas to evaporate and remove around 50% of the remaining polymerization solvent. Then, a water-soluble conditioning solution, composed of 30 wt.% N-methyl-2-pyrrolidone organic solvent and 5 wt.% CaCl₂ inorganic salt, at a temperature of 40°C was injected into the fiber, maintaining residual water content in the fiber of about 13%. Continuing the process, the fiber in contact with the conditioning solution underwent drawing at a draw ratio of 4.0, followed by washing, drying, and heating steps, ultimately resulting in the production of para-aramid fiber. [53]. DuPont developed the dry spinning method for Nomex fibers using dimethylformamide (DMF) and dimethylacetamide (DMAc) solutions. Nomex, originating from the m-aramid polymer solution, lacks the orientation observed in the solution state, in contrast to p-aramid fibers like Kevlar. Although the fibers undergo a degree of orientation during extrusion, their strength is inferior to that of their p-aramid counterparts. Augmenting the shear rate through the spinneret capillary can enhance fiber orientation; however, this leads to inhomogeneity due to solvent diffusion and the formation of a skin layer resulting from rapid solvent evaporation at the surface compared to the bulk. To improve their physical properties, the as-spun fibers are drawn, with typical mechanical characteristics in the range of 0.6 GPa and a 30% elongation at break[17].

6.2 Wet spinning

The study delves into void formation and fibrillar structure in wet-spun fibers, identifying three causes for large voids over 1 micron: polymer cracking during shrinkage, non-solvent penetration through defects, and internal coagulation due to trapped solvent domains. Smaller voids (<1 micron) result from polymer phase separation during wet-spinning. As fibers shrink and elongate, voids coalesce, aligning molecules into fibrils, notably in polymers with strong intermolecular bonding. The complex coagulation process, modelled analytically for many systems, faces limitations in predicting final structures. Utilizing Monte-Carlo simulations, Termonia explores the final membrane structure of MPIA in NMP after coagulation in water/NMP-CaCl₂ mixtures. Simulations propose achieving a dense, macrovoid-free membrane by slowing coagulation with 35-49% solvent addition, complemented by CaCl₂ to prevent macrovoids without significant coagulation slowdown. Certain polymers, like cellulose acetate existing as macromolecular aggregates, exhibit increased aggregate size with a weak solvent system during coagulation. Termonia's simulations show that adding both solvent and CaCl₂ during wet-spinning isotropic aramid copolymers with rigid monomer repeat units achieves dense, void-free fiber structures[54], [55].

6.3 Dry jet wet spinning

In solution spinning, the dope is extruded through a spinneret under heat and pressure, entering a coagulation bath. Crystal domains align along the extensional shear direction

produced by capillary extrusion, causing an interesting transition of crystal domains to deorient at the die exit. This can be overcome by filament attenuation under spinning tension, resulting in crystalline, high-modulus fibers after washing and drying. Wet spinning exposes the dope to the coagulation bath immediately, preventing complete attenuation and producing fibers with low tenacity and intermediate modulus. Dry-jet wet spinning, preferred for AFs production, allows easy separation of optimal thermal conditions for flow, spinning, and coagulation [6].

Post-spinning heat treatment under tension enhances modulus, crystallinity, and orientation, setting AFs apart from other high-performance fibers in industrial applications. Heat treatment effects increase exponentially with temperatures and draw ratio, starting around the polymer's glass transition temperature ($\sim 360^\circ\text{C}$) and peaking around the melting temperature ($\sim 550^\circ\text{C}$). Enhanced crystallinity, structure perfection, and orientation occur during heat treatment. Stretched fibers maintain high orientation, leading to a high degree of crystallinity. Dry-jet-spun yarns show a modulus jump at temperatures above 200°C , independent of temperature. The final properties of nascent fibers strongly depend on polymer structure and spinning method [6].

6.4 Electrospinning

Electrospinning is widely recognised as the most promising method for producing polymeric nanofibers. The process involves using a uniform spinning solution, which is then extruded into nanofibers through electrospinning equipment under an electric field. While recent studies have primarily focused on preparing meta-aramid nanofibers (mANF) through electrospinning in a dimethylacetamide (DMAc)/LiCl system, the electrospinning of aromatic polyamide (PPTA) fibers presents challenges due to the need for concentrated sulfuric acid (H_2SO_4) as a solvent. Attempts to electro-spin ANF in a PPTA/ H_2SO_4 solution at high temperature (85°C) and high voltage (25 kV) resulted in difficulties controlling the process, leading to branched ANF with a wide diameter distribution (275 nm–15 μm). The concentration of the PPTA/ H_2SO_4 solution significantly influenced the diameter and its distribution. To address issues related to high voltages and volatile carrier solvents in traditional electrospinning, an immersion rotary jet-spinning (iRJS) approach has been proposed. iRJS applies high centrifugal forces instead of high voltage to extrude polymer dopes into nanofiber-forming jets, allowing for tailored control over ANF diameter. While iRJS has made progress in controlling ANF size and yield compared to traditional electrospinning, it has drawbacks such as high energy consumption, larger fiber sizes (500–1000 nm), and equipment corrosion. Overall, electrospinning from a dissolved PPTA/ H_2SO_4 solution appears impractical for obtaining ANF [60].

7. Applications

Due to their distinctive characteristics, including high strength, low density, compressive strength, low flammability, absence of a melting point (direct degradation above 500°C), and excellent resistance to impact, abrasion, and chemical and thermal degradation, aramids find widespread applications in both reinforcement and apparel-related contexts [53]. However, the specific applications of m-aramid and p-aramid vary due to differences in their properties. M-aramid, exemplified by Nomex, exhibits excellent thermal resistance and textile properties but has inferior mechanical properties for high-performance fibers. Consequently, it is commonly employed in protective clothing, hot gas filters, industrial-coated fabrics, felt scrims, and the reinforcement of rubberized belts and hoses. In contrast, p-aramid, represented by Kevlar, displays unique combinations of toughness, exceptionally high tenacity and modulus, and outstanding thermal stability. As a result, p-aramid is utilized in diverse end-use sectors, including industrial, aerospace, military, and civilian applications, for purposes such as cut, heat, and ballistic-resistant apparel, hard armors, brake and transmission friction components, reinforced tyres and rubber goods, ropes and cables, various composite forms, industrial gloves, and circuit board reinforcements.

8 Conclusion

Addressing these challenges necessitates the development of a green, efficient, simple, and cost-effective synthetic method. This involves identifying low-toxicity or non-toxic solvents and new catalysts for polymerization. Improvements in monomer synthesis, processes yielding AFs with enhanced properties, and advancements in the spinning process are crucial. A universal approach is needed to rectify defects in AFs, enabling their broader application in various fields such as electromagnetic interference (EMI), electrochemical sensors, lithium-ion battery separators, and nanofiltration. These functional applications represent important directions for future AF and AF-based composite development, overcoming the limitations of conventional materials and meeting the demands of diverse industries. Maximizing the multifunctional potential of AFs requires multidisciplinary research in chemistry, physics, mathematics, computer science, engineering, and material science. This approach is essential for developing new fabrication strategies and processes, resulting in high-performance and multifunctional AFs integrated into various high-tech devices. In summary, the development of fundamental science and advanced manufacturing technologies for AFs and their composites is anticipated to drive the short-term advancement of high-end equipment, with subsequent applications in energy, electronics, environmental resources, and space exploration.

References

- [1] J. M. García, F. C. García, F. Serna, and J. L. de la Peña, "High-performance aromatic polyamides," *Prog Polym Sci*, vol. 35, no. 5, pp. 623–686, May 2010, doi: 10.1016/j.progpolymsci.2009.09.002.
- [2] M. Lv, F. Zheng, Q. Wang, T. Wang, and Y. Liang, "Friction and wear behaviors of carbon and aramid fibers reinforced polyimide composites in simulated space environment," *Tribol Int*, vol. 92, pp. 246–254, Dec. 2015, doi: 10.1016/j.triboint.2015.06.004.
- [3] F. Wang, Y. Wu, Y. Huang, and L. Liu, "Strong, transparent and flexible aramid nanofiber/POSS hybrid organic/inorganic nanocomposite membranes," *Compos Sci Technol*, vol. 156, pp. 269–275, Mar. 2018, doi: 10.1016/j.compscitech.2018.01.016.
- [4] Huaixi Wang, Huimin Xie, Zhenxing Hu, Dan Wu, and Pengwan Chen, "The influence of UV radiation and moisture on the mechanical properties and microstructure of single Kevlar fibre using optical methods," *Polymer Degradation and Stability* 97, pp. 1755–1761, 2012.
- [5] Amesimeku J, Song WH, and Wang CX, "Fabrication of electrically conductive and improved UV-resistant aramid fabric via bioinspired polydopamine and graphene oxide coating.," *J Text Inst.*, pp. 110–1484, 2019.
- [6] A. He et al., "Advanced Aramid Fibrous Materials: Fundamentals, Advances, and Beyond," *Advanced Fiber Materials*, Oct. 2023, doi: 10.1007/s42765-023-00332-1.
- [7] M. Ertekin, "Aramid fibers," in *Fiber Technology for Fiber-Reinforced Composites*, Elsevier, 2017, pp. 153–167. doi: 10.1016/B978-0-08-101871-2.00007-2.
- [8] D. Tabuani, O. Monticelli, H. Komber, and S. Russo, "Preparation and Characterisation of Pd Nanoclusters in Hyperbranched Aramid Templates to be used in Homogeneous Catalysis," *Macromol Chem Phys*, vol. 204, no. 12, pp. 1576–1583, Aug. 2003, doi: 10.1002/macp.200350027.
- [9] S. Russo, A. Boulares, A. Da Rin, A. Mariani, and M. E. Cosulich, "Hyperbranched aramids by direct polyamidation of two reactant systems: Synthesis and properties," *Macromol Symp*, vol. 143, no. 1, pp. 309–321, Aug. 1999, doi: 10.1002/masy.19991430123.
- [10] J. Liang et al., "The Effects of Polyethylene Glycol on the Spinnability of Dry-jet Wet Spinning Heterocycle Aramid Fiber," *Fibers and Polymers*, vol. 24, no. 11, pp. 3861–3867, Nov. 2023, doi: 10.1007/s12221-023-00363-w.
- [11] I. V Tikhonov, A. V Tokarev, S. V Shorin, V. M. Shchetinin, T. E. Chernykh, and V. G. Bova, "CHEMISTRY AND TECHNOLOGY OF CHEMICAL FIBRES RUSSIAN ARAMID FIBRES: PAST ----- PRESENT ----- FUTURE*," 2013.
- [12] P. W. Morgan, "Synthesis and Properties of Aromatic and Extended Chain Polyamides," *Macromolecules*, vol. 10, no. 6, pp. 1381–1390, Nov. 1977, doi: 10.1021/ma60060a040.
- [13] P. J. Flory, "Statistical thermodynamics of semi-flexible chain molecules," *Proc R Soc Lond A Math Phys Sci*, vol. 234, no. 1196, pp. 60–73, Jan. 1956, doi: 10.1098/rspa.1956.0015.
- [14] Y. Abe and K. Yabuki, "Lyotropic Polycondensation including Fibers," in *Polymer Science: A Comprehensive Reference*, Elsevier, 2012, pp. 469–495. doi: 10.1016/B978-0-444-53349-4.00150-3.
- [15] L. G. Close, R. E. Fornes, and R. D. Gilbert, "A ¹³C NMR study of mesomorphic solutions of poly(p-phenylene terephthalamide)," *Journal of Polymer Science: Polymer Physics Edition*, vol. 21, no. 9, pp. 1825–1837, Sep. 1983, doi: 10.1002/pol.1983.180210918.
- [16] W. Black and J. Preston, *High-modulus wholly aromatic fibers: Papers*. New York: M. Dekker, 1973.
- [17] M. Jassal, A. K. Agrawal, D. Gupta, and K. Panwar, "Aramid Fibers," in *Handbook of Fibrous Materials*, Wiley, 2020, pp. 207–231. doi: 10.1002/9783527342587.ch8.
- [18] E. L. Wittbecker and P. W. Morgan, "Interfacial polycondensation. I.," *Journal of Polymer Science*, vol. 40, no. 137, pp. 289–297, Nov. 1959, doi: 10.1002/pol.1959.1204013701.
- [19] M. P. W., "Condensation Polymers: By Interfacial and Solution Methods. Von P. W. Morgan. John Wiley & Sons, New York London-Sydney 1965. 1. Aufl., XVIII, 561 S., zahlr. Abb., mehrere Tab., geb. £ 9.10.-," *Interscience Publishers*, p. 787, 1965, doi: 10.1002/ange.19660781632.
- [20] S. L. Kwolek, P. W. Morgan, J. R. Schaeffgen, and L. W. Gulrich, "Synthesis, Anisotropic Solutions, and Fibers of Poly(1,4-benzamide)," *Macromolecules*, vol. 10, no. 6, pp. 1390–1396, Nov. 1977, doi: 10.1021/ma60060a041.
- [21] N. Li, X.-K. Zhang, J.-R. Yu, Y. Wang, J. Zhu, and Z.-M. Hu, "Synthesis and Characterization of Easily Colored Meta-aramid Copolymer Containing Ether Bonds," *Chinese Journal of Polymer Science*, vol. 37, no. 3, pp. 227–234, Mar. 2019, doi: 10.1007/s10118-019-2200-9.
- [22] M. Afshari, D. J. Sikkema, K. Lee, and M. Bogle, "High Performance Fibers Based on Rigid and Flexible Polymers," *Polymer Reviews*, vol. 48, no. 2, pp. 230–274, May 2008, doi: 10.1080/15583720802020129.
- [23] F. Higashi, M. Goto, and H. Kakinoki, "Synthesis of polyamides by a new direct polycondensation reaction using triphenyl phosphite and lithium chloride," *Journal of Polymer Science: Polymer Chemistry Edition*, vol. 18, no. 6, pp. 1711–1717, Jun. 1980, doi: 10.1002/pol.1980.170180606.
- [24] H. R. Kricheldorf, B. Schmidt, and R. Buerger, "New polymer syntheses. 67. Kevlar-type polyaramides of monosubstituted terephthalic acids," *Macromolecules*, vol. 25, no. 20, pp. 5465–5470, Sep. 1992, doi: 10.1021/ma00046a053.
- [25] T. Zhang, G. H. Luo, F. Wei, Y. Y. Lu, W. Z. Qian, and X. L. Tuo, "A novel scalable synthesis process of PPTA by coupling n-pentane evaporation for polymerization heat removal," *Chinese Chemical Letters*, vol. 22, no. 11, pp. 1379–1382, Nov. 2011, doi: 10.1016/j.ccllet.2011.05.037.
- [26] S. Ozawa, Y. Nakagawa, K. Matsuda, T. Nishihara, and H. Yunoki, "Novel aromatic copolyamides prepared from 3,4'-diphenylene type diamines, and shaped articles therefrom," 1978
- [27] H. Matsuda, T. Asakura, and Y. Nakagawa, "Sequence Analysis of Technora (Copolyamide of Terephthaloyl Chloride, p -Phenylenediamine, and 3,4'-Diaminodiphenyl Ether) Using ¹³C NMR," *Macromolecules*, vol. 36, no. 16, pp. 6160–6165, Aug. 2003, doi: 10.1021/ma034670b.
- [28] S. Hayashida, "Technora® Fiber: Super Fiber from the Isotropic Solution of Rigid-Rod Polymer," in *High-Performance and Specialty Fibers*, Tokyo: Springer Japan, 2016, pp. 149–169. doi: 10.1007/978-4-431-55203-1_9.
- [29] R. Simonutti, A. Mariani, P. Sozzani, S. Bracco, M. Piacentini, and S. Russo, "Poly(p-phenyleneterephthalamide)-Based Nanocomposites Obtained by Matrix Polycondensation. Synthesis and Solid-State NMR Characterization," *Macromolecules*, vol. 35, no. 9, pp. 3563–3568, Apr. 2002, doi: 10.1021/ma010007g.

- [30] F. Higashi and Y. Taguchi, "Aromatic polyamides by phosphorylation reaction with triphenylphosphite and LiCl in the presence of polymer matrix," *Journal of Polymer Science: Polymer Chemistry Edition*, vol. 18, no. 9, pp. 2875–2877, Sep. 1980, doi: 10.1002/pol.1980.170180911.
- [31] F. Higashi, S. Ogata, and Y. Aoki, "High-molecular-weight poly(p-phenyleneterephthalamide) by the direct polycondensation reaction with triphenyl phosphite," *Journal of Polymer Science: Polymer Chemistry Edition*, vol. 20, no. 8, pp. 2081–2087, Aug. 1982, doi: 10.1002/pol.1982.170200811.
- [32] F. M. Silver, "Aromatic polyamides. IV. A novel synthesis of sulfonated poly(para-phenyleneterephthalamide): Polymerization of terephthalic acid and para-phenylenediamine in sulfur trioxide," *Journal of Polymer Science: Polymer Chemistry Edition*, vol. 17, no. 11, pp. 3519–3533, Nov. 1979, doi: 10.1002/pol.1979.170171110.
- [33] Y. Shoji, K. Mizoguchi, and M. Ueda, "Synthesis of Aramids by Polycondensation of Aromatic Dicarboxylic Acids with Aromatic Diamines Containing Ether Linkages," *Polym J*, vol. 40, no. 8, pp. 680–681, Aug. 2008, doi: 10.1295/polymj.PJ2008051.
- [34] M. Li et al., "One-step synthesis of poly(methacrylate)-b-polyester via 'one organocatalyst, two polymerizations,'" *Polym Chem*, vol. 12, no. 35, pp. 5069–5076, 2021, doi: 10.1039/D1PY00892G.
- [35] A. J. Teator, D. N. Lastovickova, and C. W. Bielawski, "Switchable Polymerization Catalysts," *Chem Rev*, vol. 116, no. 4, pp. 1969–1992, Feb. 2016, doi: 10.1021/acs.chemrev.5b00426.
- [36] M. Yoneyama, M. Kakimoto, and Y. Imai, "Novel synthesis of aromatic polyamides by palladium-catalyzed polycondensation of aromatic dibromides, aromatic diamines, and carbon monoxide," *Macromolecules*, vol. 21, no. 7, pp. 1908–1911, Jul. 1988, doi: 10.1021/ma00185a004.
- [37] R. J. Perry, S. R. Turner, and R. W. Blevins, "Synthesis of linear, high-molecular-weight aromatic polyamides by the palladium-catalyzed carbonylation and condensation of aromatic diiodides, diamines, and carbon monoxide," *Macromolecules*, vol. 26, no. 7, pp. 1509–1513, Mar. 1993, doi: 10.1021/ma00059a005.
- [38] S. Peleteiro, S. Rivas, J. L. Alonso, V. Santos, and J. C. Parajó, "Furfural production using ionic liquids: A review," *Bioresour Technol*, vol. 202, pp. 181–191, Feb. 2016, doi: 10.1016/j.biortech.2015.12.017.
- [39] Y. S. Vygodskii, E. I. Lozinskaya, and A. S. Shaplov, "Ionic Liquids as Novel Reaction Media for the Synthesis of Condensation Polymers," *Macromol Rapid Commun*, vol. 23, no. 12, pp. 676–680, Aug. 2002, doi: 10.1002/1521-3927(20020801)23:12<676::AID-MARC676>3.0.CO;2-2.
- [40] E. I. Lozinskaya, A. S. Shaplov, and Ya. S. Vygodskii, "Direct polycondensation in ionic liquids," *Eur Polym J*, vol. 40, no. 9, pp. 2065–2075, Sep. 2004, doi: 10.1016/j.eurpolymj.2004.05.010.
- [41] S. Dewilde, T. Vander Hoogerstraete, W. Dehaen, and K. Binnemans, "Synthesis of poly-p-phenylene terephthalamide (PPTA) in ionic liquids," *ACS Sustain Chem Eng*, vol. 6, no. 1, pp. 1362–1369, Jan. 2018, doi: 10.1021/acssuschemeng.7b03727.
- [42] S. Dewilde, J. Winters, W. Dehaen, and K. Binnemans, "Polymerization of PPTA in Ionic Liquid/Cosolvent Mixtures," *Macromolecules*, vol. 50, no. 8, pp. 3089–3100, Apr. 2017, doi: 10.1021/acs.macromol.7b00579.
- [43] P. Wang, K. Wang, J. Zhang, and G. Luo, "Non-aqueous suspension polycondensation in NMP-CaCl₂/paraffin system — A new approach for the preparation of poly(p-phenylene terephthalamide)," *Chinese Journal of Polymer Science*, vol. 33, no. 4, pp. 564–575, Apr. 2015, doi: 10.1007/s10118-015-1607-1.
- [44] N. Zhu, X. Hu, Z. Fang, and K. Guo, "Chemoselective Polymerizations," *Prog Polym Sci*, vol. 117, p. 101397, Jun. 2021, doi: 10.1016/j.progpolymsci.2021.101397.
- [45] Z. Qiu, L. Zhao, and L. Weatherley, "Process intensification technologies in continuous biodiesel production," *Chemical Engineering and Processing: Process Intensification*, vol. 49, no. 4, pp. 323–330, Apr. 2010, doi: 10.1016/j.cep.2010.03.005.
- [46] H. Zhao, J.-X. Wang, Q.-A. Wang, J.-F. Chen, and J. Yun, "Controlled Liquid Antisolvent Precipitation of Hydrophobic Pharmaceutical Nanoparticles in a Microchannel Reactor," *Ind Eng Chem Res*, vol. 46, no. 24, pp. 8229–8235, Nov. 2007, doi: 10.1021/ie070498e.
- [47] J. Wagner, T. Kirner, G. Mayer, J. Albert, and J. M. Köhler, "Generation of metal nanoparticles in a microchannel reactor," *Chemical Engineering Journal*, vol. 101, no. 1–3, pp. 251–260, Aug. 2004, doi: 10.1016/j.cej.2003.11.021.
- [48] H. Shi, K. Nie, B. Dong, M. Long, H. Xu, and Z. Liu, "Recent progress of microfluidic reactors for biomedical applications," *Chemical Engineering Journal*, vol. 361, pp. 635–650, Apr. 2019, doi: 10.1016/j.cej.2018.12.104.
- [49] J. Kobayashi, Y. Mori, and S. Kobayashi, "Multiphase Organic Synthesis in Microchannel Reactors," *Chem Asian J*, vol. 1, no. 1–2, pp. 22–35, Jul. 2006, doi: 10.1002/asia.200600058.
- [50] J. Yoshida, A. Nagaki, T. Iwasaki, and S. Suga, "Enhancement of Chemical Selectivity by Microreactors," *Chem Eng Technol*, vol. 28, no. 3, pp. 259–266, Mar. 2005, doi: 10.1002/ceat.200407127.
- [51] X. Shi et al., "Visible-light photooxidation of benzene to phenol in continuous-flow microreactors," *Chemical Engineering Journal*, vol. 420, p. 129976, Sep. 2021, doi: 10.1016/j.cej.2021.129976.
- [52] P. Wang, K. Wang, J. Zhang, and G. Luo, "Preparation of poly(p-phenylene terephthalamide) in a microstructured chemical system," *RSC Adv*, vol. 5, no. 79, pp. 64055–64064, 2015, doi: 10.1039/C5RA10275H.
- [53] T. Park, B. Lee, J. Lee, Y. Park, and K. Rho, "Method of dry-spinning para-aramid fiber," US9976234B2, 2018
- [54] A. Ziabicki, *Fundamentals of fibre formation : the science of fibre spinning and drawing*. New York: John Wiley & Sons, 1976.
- [55] M. A. Frommer, R. Matz, and U. Rosenthal, "Mechanism of Formation of Reverse Osmosis Membranes. Precipitation of Cellulose Acetate Membranes in Aqueous Solutions," *Product R&D*, vol. 10, no. 2, pp. 193–196, Jun. 1971, doi: 10.1021/i360038a017.
- [56] D. R. Paul, "Spin orientation during acrylic fiber formation by wet-spinning," *J Appl Polym Sci*, vol. 13, no. 5, pp. 817–826, May 1969, doi: 10.1002/app.1969.070130501.
- [57] I. M. Ward, Ed., *Structure and Properties of Oriented Polymers*. Springer Netherlands, 2012.
- [58] Moreland and J. C., "Production and Characterization of Aramid Copolymer Fibers for use in Cut Protection," *Clemson University ProQuest Dissertations Publishing*, 2010.
- [59] C. Hahn, "Characteristics of p-Aramid Fibers in Friction and Sealing Materials," *Journal of Industrial Textiles*, vol. 30, no. 2, pp. 146–165, Oct. 2000, doi: 10.1177/152808370003000205.
- [60] H. J. Oh et al., "Synthesis and characterization of spider-web-like electrospun mats of meta-aramid," *Polymer International*, vol. 61, no. 11, Wiley, pp. 1675–1682, Jun. 27, 2012, doi: 10.1002/pi.4260.