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A Mini-Review of Microstructural Control during Composite Fiber Spinning

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Abstract:

From wool to Kevlar, one-dimensional (1D) fiber has experienced the transition from clothing materials to structural applications in the past centuries. However, the recent advancements in tooling engineering and manufacturing processes have attracted much attention from both academia and industry to fabricate novel, versatile fibers with unique microstructures and unprecedented properties. This mini-review focuses on the fabrication techniques of porous, coaxial, layer-by-layer, and segmented fibers with continuous solution and melt fiber spinning methods. In each section of this review article, the unique structure-related applications, including intelligent devices, healthcare devices, energy storage systems, wearable electronics, and sustainable products, are discussed and evaluated. Finally, the combination of additive manufacturing (AM) for 1D fiber patterning in two-dimensional (2D) and three-dimensional (3D) devices, in addition to challenges in the reviewed fiber microstructures, is briefly introduced in the conclusion section.

1. Introduction.

One-dimensional (1D) fibers offer fascinating features, such as flexibility, large aspect ratio and high surface area, wearability, and inherent anisotropic characteristics. As early as 4000 years ago, humans have developed fabrics based on plants and animals, such as cotton, silk, hemp, wool, and fur.[1] Their delicate nature restrained applications primarily to clothing and aesthetic purposes. The evolution of humanity and the need for advanced materials have urged researchers to synthesize much more durable artificial fibers from natural or synthesized materials, including rayon, nylon, spandex, polylactic acid (PLA), polybenzimidazole (PBI), and aramid fibers.[2–4] With the fast development of polymer science and nanotechnology since the mid-20th century, high specific strength and toughness polymer/nanoparticle fibers began to challenge other existing structural materials, e.g., metallic fibers used in aerospace and automotive fields.[5–7]

Since the beginning of the 21st century, composite fibers with complex hierarchies or architectures have grown beyond the traditional uniform/homogeneous structures. By searching keywords "core-shell structure" and "fiber", Google Scholar shows 342 publications from 1995 to 2000. This number increased to 16400 between 2015 and 2020 **(Figure 1a)**. Other structures, including porous, coaxial, layer-by-layer, and segmented morphologies (**Figure 1b**), show similar increasing trends based on Google Scholar keywords search. Such evolved fiber geometric features enabled multimaterial fibers for applications ranging from energy storage devices, smart systems, wearable electronics, healthcare to sustainable products.[8–12] One major driving force is the advancement in the manufacturing process and tooling engineering. For instance, Sochol and his group integrated rigid and compliant materials to form a shape morphing spinneret in response to pneumatic input, reconstructing nanoparticle orientations during the fiber extrusion process for unique biomedical applications.[13] Their intricate spinneret design was through Polyjet 3D printing that conventional tooling engineering finds time-consuming and expensive.[14] Other additive manufacturing methods of selective laser sintering (SLS), stereolithography (SLA), and fused deposition modeling (FDM) have all contributed to the user customization of spinneret design for highly unique fiber microstructures and applications.[15–18]

This mini-review focuses on two primary fabrication methods, solution spinning and melt spinning, which produce continuous micro-scale fibers (diameter between 1 to 1000 μm). Electrospinning and centrifugal spinning are also capable of generating versatile fiber structures. However, their fiber sizes are usually in the nanometer regime and will not be covered in this review. Readers can refer to recently published reviews by Schiffman et al.[19] , Duan et al.[20] and Bligh et al.[21] for electrospinning and Chang et al.[22] for centrifugal spinning. For the purpose of simplicity, we only focus on one-step continuous fiber spinning techniques rather than combinations between fiber spinning and dip coating,[23,24] spray coating,[25] or manual assembly processes.[26,27]

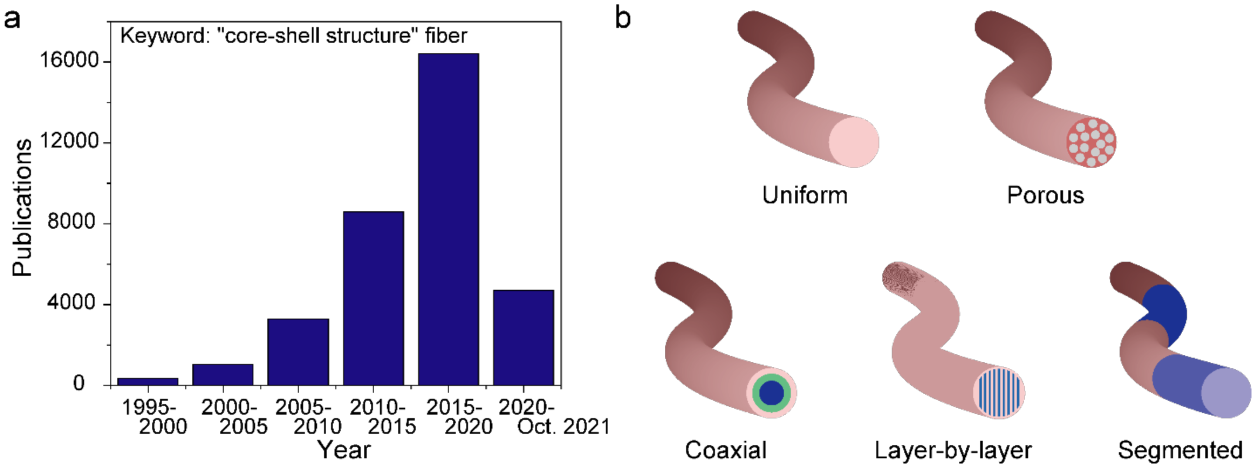

Figure 1. (a) The number of publications based on google scholar search with keywords: "core-shell structure" and "fiber" from 1995-2021. (b) Examples of microstructures in fiber materials.

2. Continuous fiber spinning techniques.

In general, continuous fiber spinning can be divided into a few categories, including melt spinning and solution spinning. Melt spinning is a process that requires melted polymer to be either thermally drawn or mechanically extruded through a tool of the spinneret, followed by procedures of cooling, solidification, and collection.[28] The solvent-free setup and fast process make it one of the most cost-efficient and environmentally friendly methods for fabricating thermoplastic materials, such as polypropylene (PP), polyethylene (PE), and nylon.[29–31] As a comparison, solution spinning is often used for polymers that degrade before melting, such as polyurethane (PU), polyacrylonitrile (PAN), and polyimide (PI).[32,33] In this method, a polymer is usually first dissolved in a solvent, followed by extrusion through a spinneret before continuous collection and post-treatment. Subcategories of solution spinning are wet and dry spinning that differ from each other in fiber solidification strategies. In wet spinning, the spinning dope travels through a coagulation bath where the solvent-nonsolvent exchange process takes place; the diffusion of the non-solvent in polymer/solvent solutions results in the precipitation of the dope into fibers. In dry spinning, the spinning dope enters an air chamber after exiting the spinneret for solvent evaporation. Via either method, the fiber gradually solidifies and is continuously collected before necessary heat-treatment, such as cold-stage drawing, hot-stage drawing, and annealing. Parameters, including post-treatment conditions, spinning dope viscosity, air-gap distance (only for dry-jet-wet spinning), drying temperature, coagulation solvent condition, and take-up speeds, are significant for fiber properties such as dimension,[34] glass transition temperature,[35] crystallinity,[36] and nanoparticle/molecular orientation[37,38]. For more comprehensive summaries on fiber spinning and material formation dynamics, readers can refer to reviews by Shang et al.,[39] Holland et al.,[40] and Puppi et al.[41]

3. Fiber microstructures.

3.1 Porous

Porosity is a vital fiber characteristic that pertains to the surface area, roughness, reactivity, absorbability, mechanical stretchability/compressibility, loading capability, and thermal conductivity, enabling applications in areas across catalysis, sensing, absorption, energy storage, and tissue engineering.[42,43] **Table 1** lists some recent works on porous fibers with associated applications and fabrication methods. The use of porogen is one of the most common methods, and the porogen types can be primarily divided into solid,[44,45] gaseous,[46] solvent,[47–49] ionic liquid,[50] and oligomeric porogen.[51] Through further etching, washing, or evaporating, porous structures can be obtained. For example, Anikeeva and her group have premixed filtered salt with polycaprolactone (PCL) for thermal fiber drawing. By rolling salt and PCL mixture around a polystyrene (PS) sacrificial core, hollow and porous PCL fiber were obtained with controllable micron-scale pore size used for microchannel nerve guidance (**Figure 2a**).[45] Nevertheless, porogen selection can be tricky and must fulfill the following criteria. First, the porogen material must be inert and does not react with the monomer or other ingredients. Second, the porogen must be compatible with the manufacturing method; solid porogen is usually associated with melt processing, and high boiling point porogen is generally preferred for solution spinning. Third, porogen must form a homogeneous and stable solution with the monomers and crosslinkers. Spontaneous phase-separation is an alternative strategy in solution spinning, which does not involve second-phase porogen materials. Both thermally induced phase separation (TIPS) or non-solvent induced phase separation (NIPS) result in polymer-rich and solvent-rich regions, forming nanometer to micrometer pores.[52–55] Another strategy of combining ice-templating with fiber spinning also eliminates the use of porogen.[56–58] Bai's group recently showed that water as the solvent gradually crystallizes by applying a cold source during fiber spinning, forming pores after freeze-drying. Interestingly, the pores were aligned with preferential direction through tuning cool source temperature and spinning speed, resulting in enhanced mechanical properties (**Figure 2b**).[59]

Table 1. Recent developed porous fiber materials.

Spinning method	Pore method	Materials	Application	ref
Thermal drawing	Porogen	NaCl, PS, PCL	Neuron growth	45
Melt spinning	Porogen	PVA, PP	Textile	60
Melt spinning	TIPS	PCL, PVDF	Ion transport	52
Dry-jet-wet spinning	Porogen	PS spheres, PS, PEG	Drug delivery	51
Dry-jet-wet spinning	NIPS	TPU, MWCNT	Organic solvents sensor	61
Wet spinning	Ice-templating	SF, chitosan	Thermal regulation	59

Wet spinning	Porous filler	rGO, MOF	Flexible battery electrode	62
Wet spinning	Porous filler	NS-GF	Supercapacitor	63
Wet spinning	Block copolymer self-assembly with phase inversion	ANMMA	Supercapacitor and oil/solvent absorption	64
Wet spinning	Hydrogel with phase separation	HPU, PPG	Tissue engineering	65
Wet spinning	Porogen and NIPS	PVDF, GO	Supercapacitor	66
Microfluidic Spinning	NIPS	PU	Self-cooling	67
Dry-jet-wet spinning	NIPS and porous filler	MgO, PEI	CO_2 capture	68
Dry-jet-wet spinning	Block copolymer self-assembly with Phase inversion	PS-b-P4VP	Ultrafiltration membranes	69

ANMMA, poly(acrylonitrile)-block-poly(methyl methacrylate); HPU, hydrophilic polyethylene glycol-based polyurethanes; MOF, metal organic framework; MWCNT, multi-walled carbon nanotube; NS-GF, nitrogen and sulfur co-doped graphene fiber; PEG, polyethylene glycol; PEI, poly(ether imide); PPG, hydrophobic polypropylene glycol; PS-b-P4VP, polystyrene-block-poly(4-vinylpyridine); PVA, polyvinyl alcohol; PVDF, polyvinylidene fluoride; rGO, reduced graphene oxide; SF, silk fibroin; TPU, thermoplastic polyurethane.

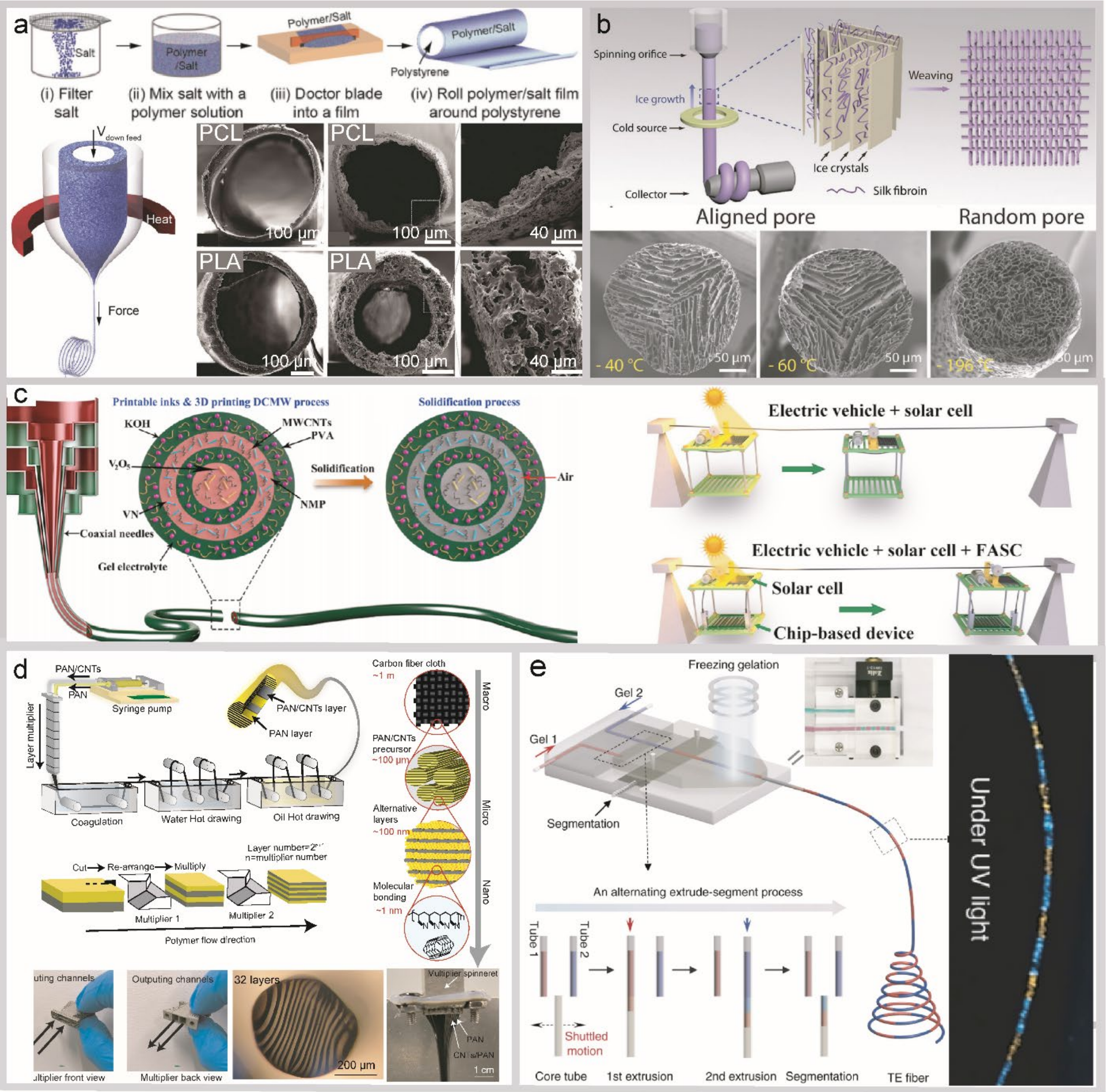

Figure 1. Advance fiber-manufacturing process. (a) Thermally drawn hollow, porous fiber of PCL and PLA with NaCl as porogen. Figure reproduced from ref. [45] (b) Ice-templating assisted wet spinning of the porous fiber. Figure reproduced from ref. [59] (c) Coaxial fiber spinning of supercapacitor with multilayer spinneret. Figure reproduced from ref. [70] (d) Forced assembly assisted dry-jet-wet spinning of alternating layers of CNT for nanoparticle alignment. Figure reproduced from ref. [71] (e) Microfluidic spinning of segmented fiber for TE application. Figure reproduced from ref. [72]

3.2 Coaxial

Coaxial structure focuses on simultaneously and concentrically fabricating two or multiple materials. Intricately designed coaxial spinneret is usually used as different materials are extruded through various inlets and merged as a single fiber upon exiting the nozzle. Each layer comprises one material for multimaterial fibers with additive functionalities, yet the multi-composition compatibility is often a challenge, especially for wet spinning methods. The solubility parameter is a good indicator to predict layer stability. Thermal drawing is an alternating method that combines different types of materials, such as polymers, metals wires, glass wires, ceramics, or semiconducting devices, through a preform step. **Table 2** lists few recent publications on coaxial structures and their material selections in each layer. The primary benefit of coaxial design includes broadening and enhancing fiber functionalities. For example, work by Zhao et al. has recently demonstrated a fiber spinning technique followed by 2D patterning of fabric supercapacitor (**Figure 2c**).[70] From the electrodes to the electrolyte, the supercapacitor consisted of four layers in a concentric structure. Compared to other fiber supercapacitors with twisted or parallel structures, the coaxial design enhanced volumetric capacity and dynamic stability.[70] Coaxial system also includes non-concentrical designs, such as parallel hydrogel electrode cores covered with electroluminescent outer layer for brain interface communications,[73] multifunctional core fiber for magnetic resonance imaging,[74] and islands and sea structure for carbon fiber.[75]

Table 2. Recent development in coaxial structure fiber materials.

Spinning method	Core materials	Shell materials	Coagulation bath	Application	Ref
Wet spinning	**Content:** Si, Ag, GO **Solvent:** water	**Content:** GO **Solvent:** Water	Chitosan solution	Li-ion battery electrode	76
Wet spinning	**Content:** CNF **Solvent:** water	**Content:** GG, CA **Solvent:** water, acetone	Ethanol	Water absorption	77
Wet spinning	**Content:** PVDF-HFP-TFE, EGaIn **Solvent:** MEK	**Content:** PVDF-HFP-TFE, PEGDA, Irgacure184 **Solvent:** MEK	Water	Self-powered sensor	78
Wet spinning	**Content:** Ecoflex, MWCNT **Solvent:** NA	**Content:** Ecoflex **Solvent:** NA	Silicone oil	Strain sensors	79
Wet spinning	**Content:** chitosan **Solvent:** acetic acid, water	**Content:** PSS **Solvent:** water	Water, ethanol	Tissue engineering	80
Wet spinning	**Content:** CNF **Solvent:** water	**Content:** CNT **Solvent:** HCL	HCL	Electronics	81
Dry-jet-wet spinning	**Content:** PAN, GnP **Solvent:** DMSO	**Content:** PAN **Solvent:** DMSO	Methanol	Mechanical	82
Dry-jet-wet spinning	**Content:** GnP **Solvent:** DMSO	**Content:** PVA **Solvent:** DMSO	Methanol	Conductive fiber	15
Thermal drawing	**Content:** COC, PE, graphite **Solvent:** NA	**Content:** PC **Solvent:** NA	N/A	Optogenetic interrogation of neural circuits	83
Melt spinning	**Content:** LLDPE, CB **Solvent:** NA	**Content:** PVDF **Solvent:** NA	N/A	Piezoelectric	84

CA, cellulose acetate; CB, carbon black; CNF, cellulose nanofiber; COC, cyclic olefin copolymer; DMSO, dimethyl sulfoxide; EGaln, eutectic gallium-indium; GG, guar gum; GnP, graphene nanoplatelet; GO, graphene oxide; HCL, hydrochloric acid; LLDPE, linear low-density polyethylene; MEK, butanone; PC, polycarbonate; PSS, polystyrene sulfonate; PVDF-HFP-TFE, poly(vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene).

3.3 Layer-by-layer

Layer-by-layer fiber is defined by incorporating different material composite layers across the fiber axis and each layer is homogeneous along the fiber direction. The first appearance of the layer-by-layer fiber can be traced back to the mid-1960s as Du Pont first introduced their Cantrece fiber, which consisted of two adjacent nylon polymers. Upon retraction, the fiber transformed into a highly coiled elastic fiber due to the mismatch in the mechanical properties.[85] Similarly, a typical application of layer-by-layer fiber is for bilayer actuation, where two adjacent materials show different responses to a stimulus.[86] Another critical aspect of layer-by-layer fiber structure is the high interface area between layers. Kinetic static mixer (KSM) and forced assembly processes can generate multilayered structures and have been developed for over decades.[87–90] However, their complicated experimental setups and sophisticated internal designs limited their potentials from lab-scale researches. With the uprising of additive manufacturing, recent work by Song's group used laser powder bed fusion (LPBF) to fabricate millimeter-scale multipliers for patterning CNTs in PAN fiber (**Figure 2d**).[71] As PAN and PAN/CNTs solutions entered the forced assembly process, they were cut horizontally and rearranged vertically, transforming two adjacent layers into four. By repeating this process, a number of 512 alternating layers of PAN and PAN/CNTs were achieved with a layer thickness of around 170 nm. The interfacial interactions between the layers resulted in superior 1D particle orientation.[71] Multilayered structures are also particularly relevant in biological applications, such as multimaterial tissue constructs. Madero et al. used digital light processing (DLP)-based 3D printing to print up to 7 KSM elements to construct a multi-lamellar architecture.[91,92] The resulting cell/hydrogel interface surface area was as high as ~100 $cm^2\ cm^{-3}$, which showed superior cell alignment and more durable cell life.[91] **Table 3** lists the recent development of layer-by-layer fibers with specific layer numbers and unique applications through these layer formations.

Table 3. Recent development in layer-by-layer fiber fabrication technique.

Spinning method	Layer method	Materials	Layer number	Application	Ref
Melt spinning	Side-by-side spinneret	PET, IPA, NPG	2	Self-crimping	93
Melt spinning	Side-by-side spinneret	EOC, PP	2	Self-crimping	94
Microfluidic spinning	PNIPAM, Ca-alginate	Ca-alginate	2	Temperature actuation	95
Microfluidic spinning	PNIPAM-AAc, Na-alginate	Na-alginate	2	Ph actuation	96
Wet spinning	KSM	GelMA, alginate, myoblast	8	Muscle construct	92
Wet spinning	KSM	sodium alginate, graphite, bacteria	64	Bioprinting	91
Wet spinning	Side-by-size spinneret and twisting	GO, CNT, VC, CMC	2	Supercapacitor	97
Dry-jet-wet spinning	Forced assembly	PAN, CNTs	512	Nanoparticle alignment	71
Thermal drawing	Preform/assembly	Cu, PVDF, CB, PC, LiTFSI, COC, CPE	5	Supercapacitor	98
Thermal drawing	Preform	P(VDF-TrFE-CFE), CPE, Bi-Sn	16	Microelectromechanical systems	99

AAC, acrylic acid; AC, activated carbon; CMC, carboxy methyl cellulose; CNT, carbon nanotube; CPE, conductive polyethylene; EOC, ethylene octene copolymer; GelMA, gelatin methacryloyl; GO, graphene oxide; IPA, isophthalic acid; LiTFSI, lithium bis(trifluoromethanesulfonyl)imide; NPG, neopentyl glycol; PET, polyethylene terephthalate; PNIPAM , poly(N-isopropylacrylamide); VC, vitamin C.

3.4 Segmented

Unlike structures mentioned above, where constant cross-sections were maintained, segmented fiber has different materials continuously aligned along its axis, leading to unique multifunctionality. For melt spinning, thermal drawing of preformed segmented raw material[100] or in-situ surface patterning techniques is used.[101] For wet spinning, the most common methods are switching input material types,[102,103] physical segmentation during fabrication,[72] and Rayleigh instability technique.[104] For example, Ho's group recently developed a scalable thermoelectric (TE) fabric composed of segmented fibers (**Figure 2e**).[72] A continuous alternating extrusion process of p-type and n-type gel solution was used, followed by freezing gelation. Low loss modulus G'' and storage modulus G' were formulated to enable gel deformation under applied pressure. By further weaving the segmented fiber into the 2D fabric, p/n-type TE segments formed successive p-n junctions between hot and cold surfaces. **Table 4** lists selected recent works on segmented fibers with various applications.

Table 4. Recent development in segmented fiber fabrication technique.

Spinning method	Segment 1 materials	Segment 2 materials	Application	Ref
Gel spinning	SWCNT, PVA	PEI, SWCNT, PVA	Thermal electric	72

Wet spinning	DA, AMPS, AAm, APS, BIS, rGO	Dragon Skin, thermochromic microcapsules	Strain and temperature sensors	103
Wet spinning	Polyalanine crystalline region	Amorphous glycine-rich region	Biomimicry	105
Dry-jet-wet spinning	Alginate	PBMC	Cell encapsulation	106
Microfluidic spinning	Alginate	Salt solution	Biomimicry	107
Microfluidic spinning	Primary rat hepatocytes	Mouse fibroblast cell line	Tissue culture	108
Microfluidic spinning	Calcium alginate	PLGA droplet	Biomimicry	109
Thermal drawing	PC	Semiconductor	Optical communication	100
Thermal drawing	PC, PVDF, PEEK	Lines, microdots, cylinders	Triboelectric nanogenerators	101

AAm, acrylamide; AMPS, 2-acrylamido-2-methyl -1-propanesulfonic acid; APS, ammonium persulfate; BIS, N,N′-methylenebis (acrylamide); DA, dopamine hydrochloride; PBMC, peripheral mononuclear cells; PEEK, polyether ether ketone; PLGA, poly(lactic-co-glycolic acid); SWCNT, single-wall carbon nanotubes.7

4. Conclusion and Future Perspective

Microstructured fibers have gained much attention as the building block for next-generation wearable electronics, smart materials, biomedical devices, energy storage systems, and sustainable products with the advancement in fabrication techniques. In terms of fiber microstructures, porous, coaxial, layer-by-layer, and segmented fibers all have unique advantages; porous fiber for high surface area-related applications, coaxial fiber for durable multimaterial based devices, layer-by-layer fiber for interface dependent interactions, and segmented fiber for multifunctions along the fiber axis. Nevertheless, there is still plenty of room to diversify the fiber microstructure, rapidly prototype hierarchies, and significantly reduce design and manufacturing costs for future research. Below are some potential research directions.

(1) For porous fiber, there is often a tradeoff between porosity and mechanical properties. Cellular-based architectures, such as honeycomb or kirigami structures, have exceptional specific mechanical strength, achieving desirable porosity and mechanical properties.[110,111] Therefore, innovative approaches for engineering designated pore distribution, pore size, and tortuosity are critical for next-generation porous fibers.

(2) For coaxial fiber spinning, the limited material selection is one of the major challenges. As shown in **Table 2**, for all wet spinning techniques, both core and shell components have the same or very similar solubility parameters to maintain a stable interface. Therefore, introducing a middle transition layer could be a viable solution, yet its layer thickness should be as small as possible to minimize any undesired effect on the overall functionalities.

(3) Layer-by-layer fiber shares similar interface instability issues compared to coaxial fibers. Furthermore, to achieve a uniform interface during layer multiplication, stable laminar flow is required. Reynolds number, *Re*, for solution stability flowing through a pipe is calculated based on **eq 1**, where ρ is the density of the fluid (kg m^{-3}), u is the velocity of the fluid (m s^{-1}), D_H is the diameter of the pipe (m), and μ is the viscosity of the fluid (Pa.s).[112]

$$R_e = \frac{\rho u D_H}{\mu} \qquad (1)$$

The current multiplier chamber dimension is around 1 cm, and to achieve a minimum *Re* number, a high μ is required (e.g., 50 Pa.s).[71] This limits solution composition, such as high polymer and nanoparticle concentrations. One of the solutions is to use 3D printing methods, such as SLA, with higher printing resolution to decrease D_H, resulting in a lenient μ requirement and broader material selection range.

(4) The segmented fiber structure is still in its early research stage as there are not many reported studies. Apart from the interfacial compatibility control difficulties that cause material failures, another possible reason could be the non-constant cross-section morphology along the fiber axis, which somewhat seems

contradictory to the fundamental mechanism of fiber spinning. Therefore, more energy-efficient segmentation methods or applications that could greatly benefit from such a structure need to be explored.

(5) The advancement in manufacturing processes flourished versatile fiber microstructures and attracted new research attentions in patterning 1D fibers through FDM or direct ink writing (DIW). FDM and DIW share similar working principles with melt and solution spinning, respectively,[113,114] resulting in transformative technologies for complex geometries, rapid prototyping, and low material waste. Various 3D printing techniques are capable of forming (i) 2D patterns composed of fibers, including meshes,[115] membranes,[116] interdigitate circuits,[117] honeycomb/cellular walls,[118] and (ii) 3D architectures with fiber content, including pillars,[119] scaffolds,[120] and complex biomimicking structures,[121,122] contributing to the expansion of manufacturing protocols for multimaterial and multifunctional device-making.

In conclusion, fibers have evolved from natural fibers to chemical fibers to composite fibers. Fiber-based devices with applications including diode, field-effect device, chemical sensing, omnidirectional mirror, stimulus-responsive, and energy harvesting are undergoing immense studies. Along with the capability of fabricating different fiber microstructures, the next generation of fiber is expected to have multiple functionalities all merged into a single monolithic device, pushing the application limits, especially in electronic devices and smart systems.

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