Advances in Melt Electrospinning Technique

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Abstract

Melt electrospinning is a technique capable of producing micro- and nanofibers with the advantages of being eco-friendly, cost-effective, and applied in many areas such as nonwovens with high performance, biomedicine, high-efficiency filtration, oil sorption, and many others. This chapter describes the current trends on melt electrospinning including advancements in the technique, processing parameters, materials, apparatus, and areas of applications. Melt differential electrospinning which is a new technique for nanofiber production invented by our innovation team of advanced polymer processing has been introduced. Future perspectives on melt electrospinning are also proposed.

Keywords

Electrospinning · Melt electrospinning · Microfibers · Nanofibers · Processing parameters · Biomedicine · Environmental protection and improvement

Introduction

Electrospinning is a unique approach using electrostatic forces to produce micro- and nanofibers from polymer solutions and melts [1]. Electrospun fibers have a small pore size and high specific surface area due to their small diameters. There is also evidence of sizable static charges in electrospun fibers that could be effectively manipulated to produce three-dimensional structures. Electrospinning is also appropriate to cover a wide range of fiber diameters from several microns to nanometer. According to earlier research results, it is evident that the average diameter of electrospun fibers ranges from 100 to 500 nm. The advantages of the electrospinning process are its technical simplicity and its easy adaptability. The equipment used for electrospinning is easily constructed. It mainly includes a high-voltage polarity, a syringe pump to supply the solution to the spinning tip, and a plate collector [2].

Since the invention of electrospinning in the early twentieth century, over 200 universities and research institutes worldwide are studying various aspects of the electrospinning process and the fiber it produces making the electrospinning research into a peak. This can be noticed from the literature statistics referred from

"SciFinder" by the keyword "electrospinning" in Fig. 1a. However, melt electrospinning only made 1% of total articles published about electrospinning as Fig. 1b showed. The total articles with melt electrospinning in the title are about 316 up to April 2017; this great gap between melt electrospinning and solution electrospinning is caused mainly by the inadequate research of the principle and apparatus of melt electrospinning. Melt electrospinning is a promising process which has several superiorities over solution electrospinning. Much of the research, industrialization, and commercial outcomes have been in solution electrospinning because of the thick fiber diameter, high viscosity, and device complexity for high temperatures and high voltage in melt electrospinning methods. A general comparison of solution electrospinning and melt electrospinning is shown in Table 1. Melt electrospinning was first described in the patent in 1936 [3], and it was not until 45 years later that other three papers described the same process [4–6]; only the first paper described for electrospinning of polymer melts, producing poly(ethylene) (PE) and poly(propylene) (PP) fibers [4]. The second and third papers investigated melt electrospinning using silicone oil as a model fluid [5] and polyethylene (PE) or Nylon 12 (N12) dissolved in hexane [6], respectively.

Melt electrospinning provides an alternative polymer processing technology where medical grade polymer can be processed "as received" from the supplier.

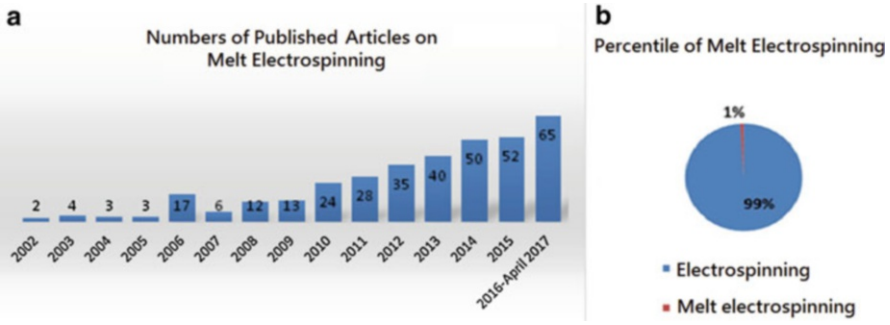

Fig. 1 (**a**) Keyword "electrospinning" in the literature statistics based on SciFinder; (**b**) the percentile of melt electrospinning in the total published articles related to electrospinning from 2002 to 2017 based on SciFinder

Table 1 Comparison of solution electrospinning and melt electrospinning

Technique	Solution electrospinning	Melt electrospinning
Solidification mechanism	Mass transfer (solvent evaporation)	Heat transfer (cooling)
Solvent-free	No	Yes
Efficiency	Lower	Higher
Environmental friendly	No	Yes
Modeling	Easier	Harder
Diameter of fibers	Smaller	Larger
Viscosity limitation	No	Yes

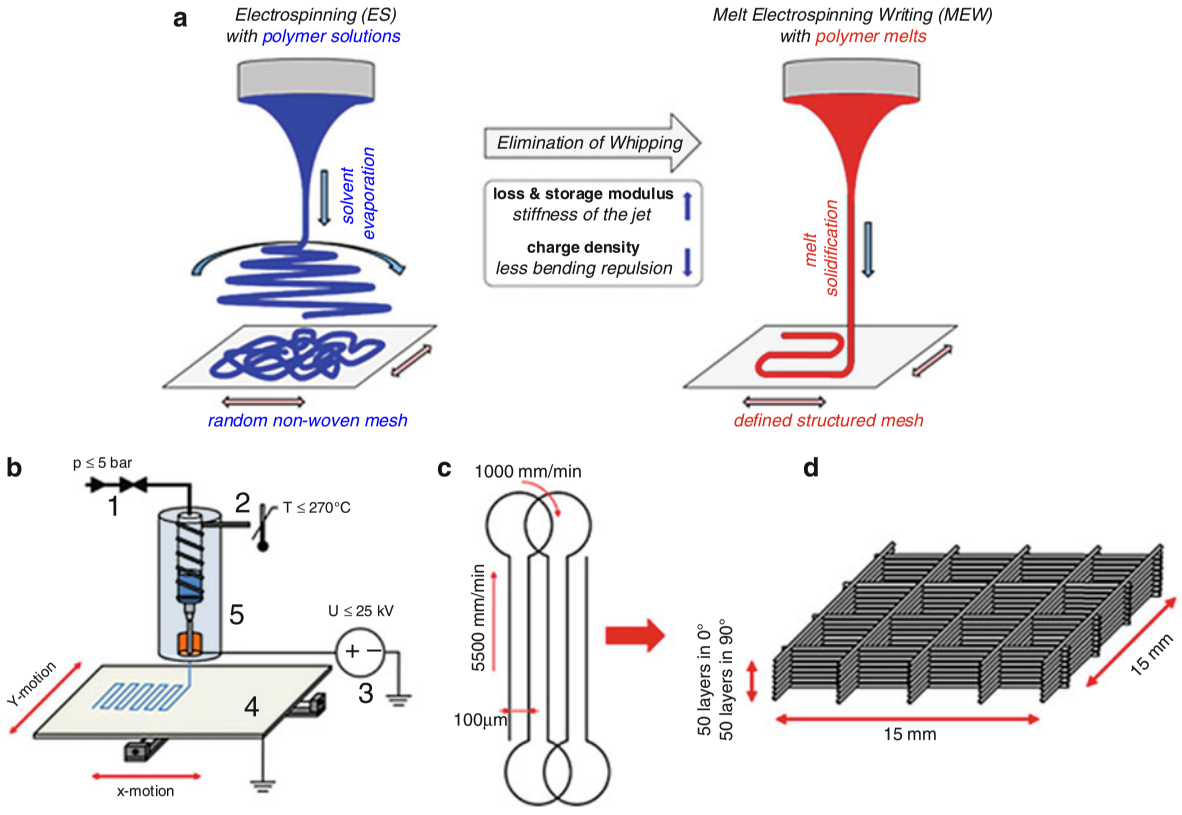

Fig. 2 Schematic of hot melt electrospinning. (**a**) Comparison shows the use of a polymer melt, instead of a polymer solution, leading to a stabilized jet and a controlled direct writing approach for fiber deposition. The melt electrospinning device (**b**) with (1) pneumatically assisted feeding system, (2) electrical heating

Recently, the biomedical community has largely embraced the rapidly emerging additive manufacturing (AM) phenomenon as Fig. 2 showed [7–9]. In solution electrospinning, fibers with consistent density and thickness could be obtained because of the residual repulsive charges around the collected fibers. However, the thickness of such substrates is often less than 1 mm. In contrast, the predictable location of the melt electrospinning jet makes this form of electrospinning to allow a direct writing method, close to AM method based on extrusion processing. The fiber morphology could be well controlled in its size, shape, and volume, however so far not obtained by solution electrospinning [10].

This chapter discusses the difference between melt electrospinning and the traditional solution electrospinning methods, including established research that describes the process through experimental observation. The differences between these two techniques will be analyzed in order to draw more attention to melt electrospinning and enlarge the advantages of the technique. Some polymers that have been melt electrospun are presented. Also, our invented melt differential electrospinning method may give researchers some hope and inspiration to realize the green manufacturing of continuous nanofiber in a massive way.

Melt Electrospinning and Its Technologization

Up to date, many researchers focused on improvement of electrospinning equipment, on fibers made from special materials and structure, and on nanoscale fibers based on test results or microscopic images. Less research work has been done on melt electrospinning because of many obstacles such as high viscosity, complicated setups, and high voltage [11–13] and also inadequate theoretical studies. Numerous works have been carried out to develop melt electrospinning process and its applications, this trend can be clearly sensed from the number of publications between 2002 and up to April 2017 (Fig. 2) based on "SciFinder" which reflects the increasing interest yearly. Lyons [14] studied the theoretical model of melt electrospinning and pointed out that the electric field strength and molecular weight have a domain effect on the morphology and diameter of melt electrospun fibers [13]. Zhmayev [15] proposed a polymer melt electrospinning with the gas-assisting process and found that the air dragging produced an additional 10% thinning compared to the pure melt electrospinning process. Christopher [16] made poly(butylene terephthalate), polypropylene, and polystyrene fiber by melt blowing apparatus with a single needle. They prepared nanofibers with average diameters smaller than 500 nm. Ogata [17], from the University of Fukui in Japan, designed a melt electrospinning setup that could produce a 1 μm fiber with laser heating source.

Fig. 2 (continued) system, (3) high-voltage source, (4) computer-aided movable collector plate, and (5) syringe with molten polymer and needle tip with the electrode. (**c**) Diagram of G-code motion path and deposition process of the filament structure. (**d**) Submicron fibers are alternately deposited in each of the 0° and 90° directions [7]

Fang et al. [18] proposed a needleless melt electrospinning device with a disc. Michal Komarek and Martinova [19] proposed two melt electrospinning devices, one has a "rod"-style spinning head and another has a slot-shaped spinning head. The slot-shaped one didn't combine the screw continuous extrusion device, and the melt distribution at the slot was poor. In addition, the number of the fibers was limited when using a slot only. The author's research group proposed melt differential electrospinning for green manufacturing of nanofiber, and the effect of voltage and temperature on fiber morphology was studied, and a few micron-grade fibers were achieved [20, 21].

Process Parameters

Material Parameters

For all electrospinning methods, material parameters such as polymer molecular weight (Mwt) and molecular chain conformation are important. Polymers of higher Mwt and a tactic nature result in thicker melt electrospun fibers due to the stronger chain entanglement, higher viscosity, and poor crystallization of the melt. Moreover, very low flow rates are needed, but the high viscous melts make nozzle blockage a problem at low flow rates [11]. Figure 3 showed different materials [22–31] have been transformed into different configurations by electrospinning process.

Melt Viscosity

Similar to solution electrospinning (Fig. 4), melt viscosity has a significant effect on spinnability of the melt. In a certain range, decreasing viscosity contributes to better spinnability, and also that melt flow index directly reflects melt viscosity. In order to electrospun using the solution, the viscosity of solution system must be in a certain range (5–20 Pa·S). In solution electrospinning, beads or beaded fiber may be obtained if the fluid is too dilute (Fig. 4). At the same, in melt electrospinning, if the viscosity of polymer melt is too small, beads will be prepared. Also, the viscosity of the melt shouldn't be too high; otherwise, the electric force can't overcome the viscosity resistance for spinning. But low viscosity due to very small molecular weight will be unable to produce fiber. The high melt viscosity is a universal problem in the melt electrospinning, which makes fiber thick or even could not be electrospun [4]. Thus, researchers are trying to use a variety of methods to reduce viscosity, to get finer fiber. As many researchers reported, the viscosity of melt ranges from 20 to 200 Pa·S [12], and in most article researchers use the melt flow index to characterize the melt viscosity, which ranges 300–2000 g/10 min.

Applied Voltage

The electrospinning process prepares fibers when the applied voltage is higher than a given value required to overcome the surface tension of the spinning fluid. In 1969

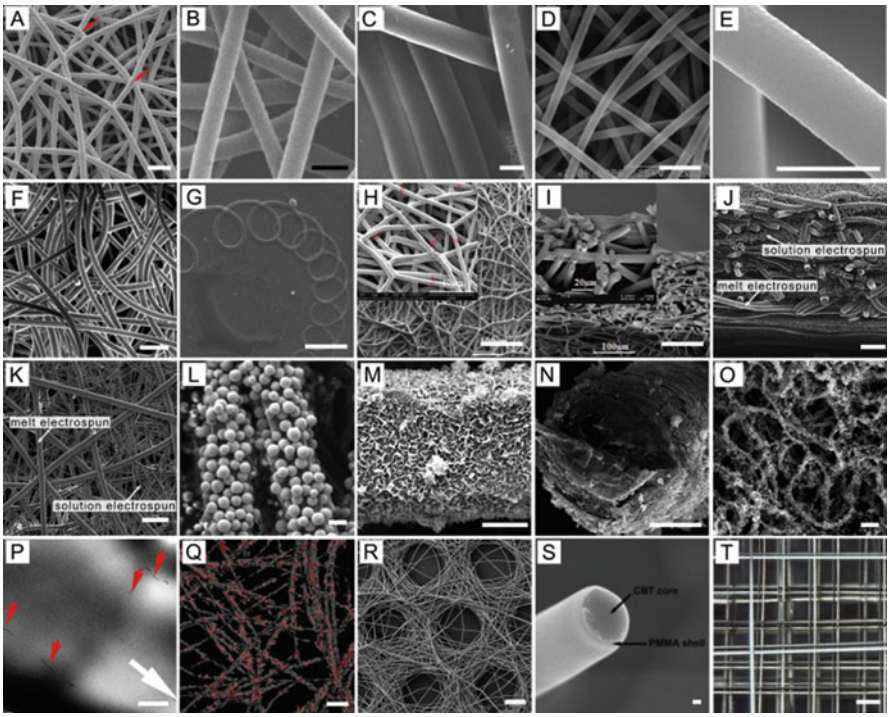

Fig. 3 Various melt electrospun materials: [10] (**a**) poly(ethylene glycol)-block-poly (ε-caprolactone) (*PEG-b-PCL*)/poly(ε-caprolactone) (*PCL*) blend fibers fused at their crossover points. Other types of nonwoven obtained by melt electrospinning are (**b**) poly-L-lactide (*PLLA*), (**c**) low-density polyethylene (*LDPE*), (**d**) poly(ethylene-co-vinyl alcohol) (*EVAL*), (**e**) gas-sensing pitch fibers, (**f**) 1,3,5-triaminobenzene, (**g**) typical nanofiber of ~100 nm in diameter, (**h**) top and (**i**) cross-sectional views of typical morphology of a nonwoven polyurethane (*PU*) fibers [23]. Multiphasic scaffolds that contain both submicron- and micron-scale fibers were produced from (**j**) poly (lactic acid) (*PLA*) [24] and (**k**) poly(lactic-co-glycolic acid) (*PLGA*) [25]. (**m**, **n**) CaP coatings are important for bone tissue engineering scaffolds and can be deposited upon poly-ε-caprolactone (*PCL*) fibers prior to cell culture [26]. (**o**) Particulates have been included, such as TiO2 melt electrospun with PP [27] and (**q**) strontium-substituted bioactive glass (red particles) within poly-ε-caprolactone (*PCL*) fibers [28]. (**r**) When using electroconductive collectors with patterned voids, the gross melt electrospun fiber morphology replicates the pattern of the conductive material, i.e., poly-ε-caprolactone (*PCL*) [29]. (**s**) Coaxial melt electrospinning of poly(methyl methacrylate) (*PMMA*) nanofibers loaded with crystal violet lactone-bisphenol A-1-tetradecanol (*CBT*) [30]. (**t**) Translating a collector allows controlled arrangement of fibers, e.g., poly(2-oxazoline) [31]. Scale bars are (**a**) 10 μm, (**h**, **i**, **j**) 100 μm, (**k**) 50 μm, (**l**) 10 μm, (**m**, **n**) 5 μm, (**o**) 10 μm, (**p**) 500 nm, (**q**) 200 μm, (**r**) 200 μm, (**s**) 100 nm, and (**t**) 100 μm

Taylor deduced the threshold voltage of electrospinning [33]. When the applied voltage exceeds this value, it breaks the balance of the electric force and the surface tension of the droplet, so a jet ejects. In 1964, Hendricks [34] also got a similar equation, suggesting that the threshold voltage is directly related to the fluid surface tension. The surface tension of low melt viscosity is nearly the same of the solution system. However, more than two times of solution electrospinning voltage is needed

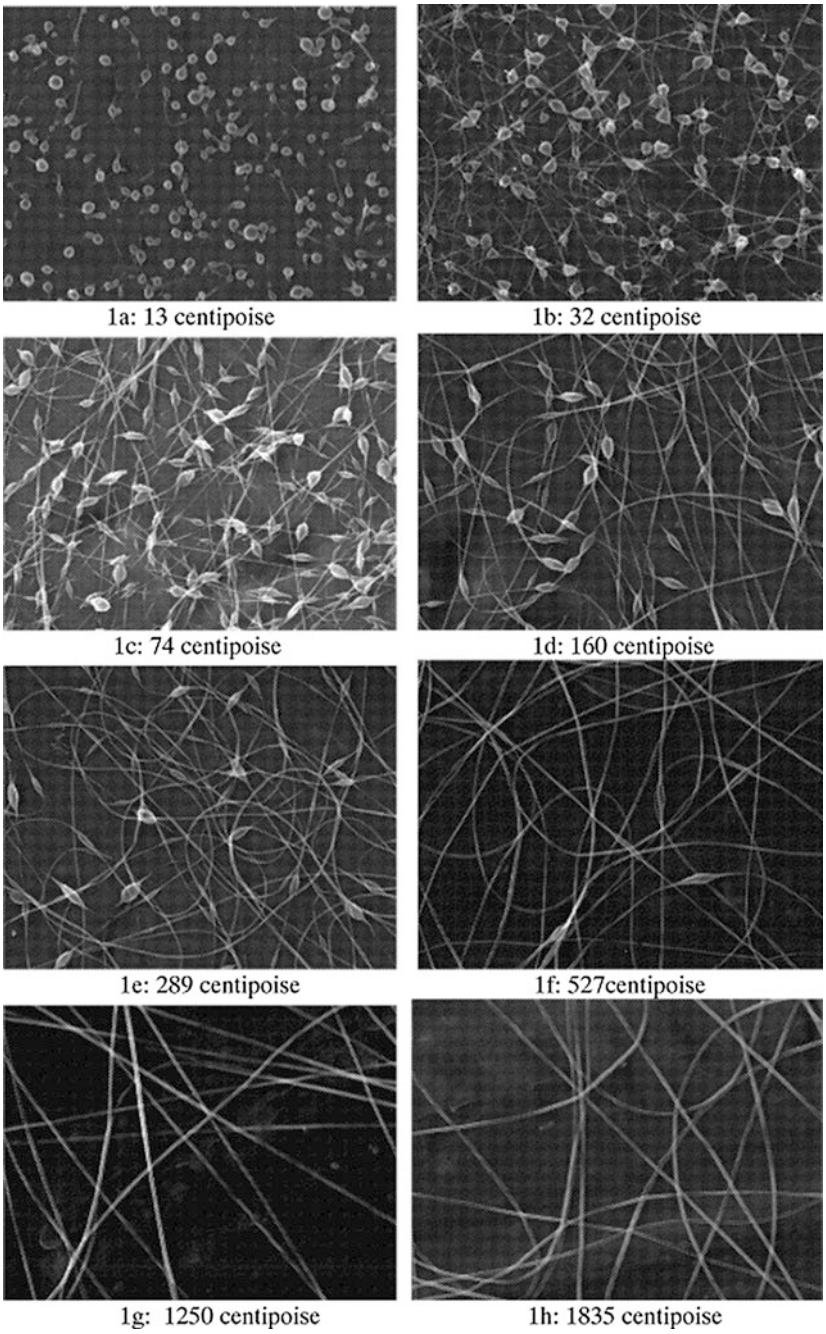

Fig. 4 The morphology of beaded fibers versus solution viscosity. The electric field is 0.7 kV/cm. The horizontal edge of each image is 20 μm long [32]

for melt electrospinning. That explains the dielectric properties of the melt, and 20–100 kV is needed to polarize the melt and induce the generation of jet [35]. Usually, 5–20 kV is loaded on the end of the syringe needle when solution electrospinning, and most of the researchers also took the same strategy. But the end of syringe needle often is where the melt is plasticized, which makes the researchers heat the melt indirectly [36–40] or use the insulating material to isolate the needle, all of which limit the diversity of the nozzle designing [41]. Some measures solving those problems will be noted below. Increasing the voltage is a common measure to obtain finer fibers, but it could cause corona or breakdown if it is too high; finally, the alarm terminates the process. Ratthapol [39] proposed vacuum melt electrospinning method, improving the threshold voltage; the load voltage can reach 1–30 kV/cm and will not breakdown; finally the finest fibers with 300 nm diameter were obtained, but the fibers need to be spun in the space in mass production scenarios.

The electrical field strength effects the deformation of the droplet on the spinning tip before the ejection of the electrospinning jet. Figure 5 shows three stages in droplet deformation as the electric field is increased. When the voltage is too small, no evident deformation happens, and the fluid on the tip is hemispheric; when the voltage is greater, the jet deforms into a conical shape, and the cone angle gets smaller with the increase of the voltage; then a jet ejects from the tip of the cone when the voltage is greater than the critical voltage.

Jet Characteristics

Melt electrospinning is different from solution electrospinning, in which jets go through both stable and unstable periods before deposition and jets almost don't whip during melt electrospinning process [25], apart from some of the low melt viscosity which also observes rotating or even whipping [42]. In solution electrospinning, it is thought that the evaporating of solvent and the whipping of the jet are the main reasons of the fiber refining [43]. And there is no solvent evaporation in melt electrospinning which greatly limits the jet refining. And the freedom of charge on the surface of the melt is not much higher than the solution, so melt cannot form unstable charge in the process of electrospinning like a solution and is not easy to generate instability.

Jet Speeds

The jet speed of melt electrospinning is much lower than that of solution spinning because of the lack of whipping process. The typical velocity of a melt electrospinning is around 1 m/min, which was tested by Hochleitner G. et al. in a near-field melt electrospinning experiment with the conditions of a 30 G spinneret at 2.5 kV acceleration voltage, 90 °C heating temperature, 1 mm collector distance, and 1.0 bar pressure [43]. The result showed the pulsing disappeared when the collect speed is greater than

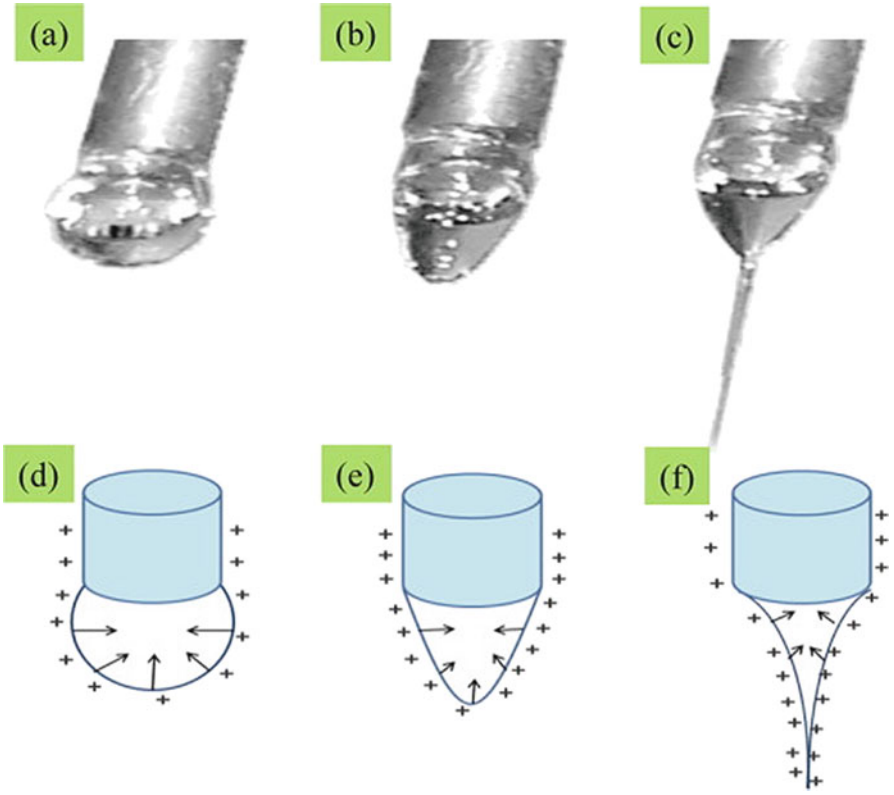

Fig. 5 (**a**–**c**) Digital images showing the three-stage deformation of a polymeric droplet under the influence of increasing electric field [42]. The cartoon (**d**–**f**) shows the mechanism of the effect of charges on the polymeric droplets. As the intensity of the electric field is increased, the hemispherical drop formed at the tip of the needle gets converted into a conical shape

the jet speed, termed the critical translation speed (CTS) (Fig. 6). This result was usually used for controlled deposition of microfiber in scaffold preparation.

Fiber Fineness

The fibrous degree of fineness influences the surface area, as well as the filtration resistance and porosity, so it indirectly determines the properties and applications of fibers. The diameter of the fibers made from solution electrospinning generally ranges from 100 to 1000 nm; the porosity is in the range of 2–465 μm [44], therefore, air can get through or penetrate things like liquid, cell or coarse particles will be blocked, as reported, most of the fibers produced using melt electrospinning have a diameter above 1 μm (Table 2) [45], some are under 1 μm by instantly

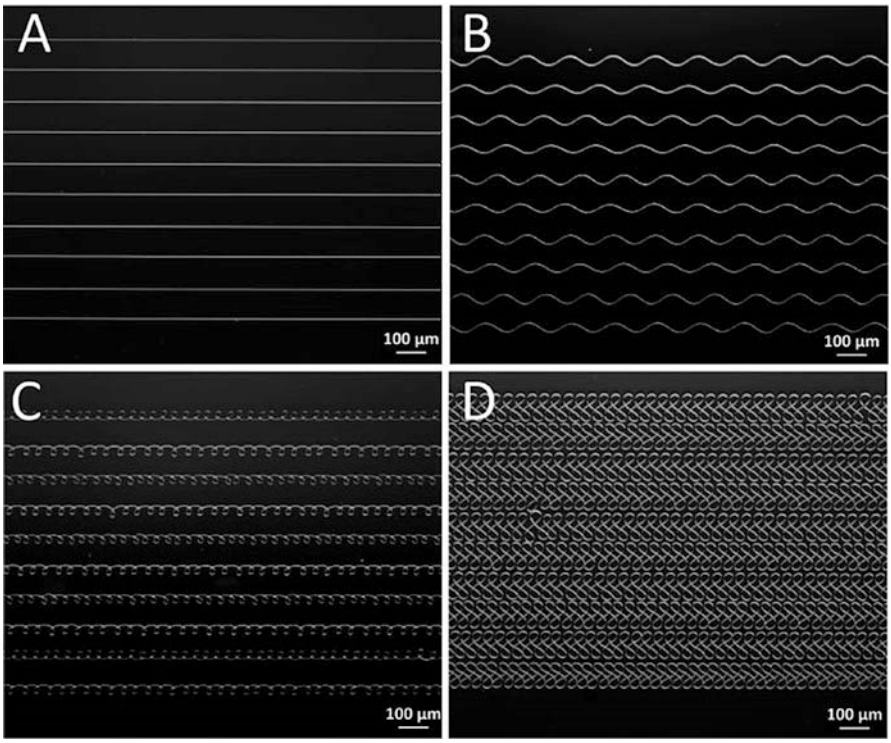

Fig. 6 Fabrication of different patterns by changes in collector speed at and below critical translation speed (*CTS*). The fibers were deposited in a series of ten lines on the collector with a 30 G spinneret at 2.5 kV acceleration voltage, 90 °C heating temperature, 1.0 mm collector distance, and 1.0 bar pressure. Fiber collection was performed at (**a**) 100–110% of CTS, (**b**) 75–80% of CTS, (**c**) 30–35% of CTS, and (**d**) 10–15% of CTS [43]

Table 2 Fiber diameters of some main polymers processed by melt electrospinning method

Polymer	Fiber diameter/µm	Flow/ $ml \cdot h^{-1}$	Process characteristics	References
Polypropylene (PP)	0.31	0.078	5% NaCl	[38]
Polyethylene (PE)	5.5–14.3	–	0.6 mm needle	[45]
Polyamide (PA)	0.9–1.8	1.2	270 °C	[46]
Polylactic acid (PLA)	0.2–0.3	0.61	Air-assisted	[47]
Thermoplastic polyurethane (TPU)	1.7–2.53	0.087	Laser heating	[48]
Polyethylene terephthalate (PET)	1.69–3.28	0.01–0.09	Laser heating	[36]
Polycaprolactone (PCL)	0.27–2.0	0.05	Air gun heating	[22]

high-temperature heating and adding viscosity thinner or inorganic salt, using air assistance can decrease the fiber diameter to 200–300 nm [46], but only limited materials are able to reach that range, and complex equipment is needed. Therefore, further researches are needed in melt electrospinning field to develop the characteristic of high fibrous strength and apply this technique in green manufacturing, as well as thinning the fiber fineness compared with solution electrospinning.

Spinning Efficiency

Most of the solution electrospinning with a single needle has the speed ranging from 0.01 to 1 mL/h, and only 1–30% of the polymer will solidify after solvent evaporation [44]. Researchers reported that the melt electrospinning with a single needle has the speed ranging from 0.1 to 1 mL/h and 100% melt convert to fiber. Even so, its efficiency is still hard to meet the requirement [49]. A series of attempts on needleless electrospinning technology to increase efficiency are listed in Table 3. Elmarco Company developed the second-generation production lines which can produce a fibrous membrane with the speed of 288 g/h. The needleless melt electrospinning can reach the speed of 12.5 g/h with one nozzle, which has a large space remaining for improvement [50]. Just like solution electrospinning, a jet of melt electrospinning has a certain corresponding feeding speed to get the fine fiber, which determines that the efficiency must be improved by increasing the amount of jet ejected from every unit area. Namely, lowering the distance between every adjoining jet as much as possible is needed for the promising degree of fibrous fineness.

Temperature and Humidity

In the process of solution electrospinning, ambient temperature and humidity influence the viscosity and speed of solvent evaporation, which has an indirect effect on

Table 3 Output of needleless melt electrospinning devices

Structure	Specific differential structure	A single yield/g h^{-1}	References
Linear type	Line laser	0.36–1.28	[51]
	Wire coating	288	Elmarco Company
Profile	Circumference curve	4.2	[52]
	Circular curve	6.85	[53]
Plane type	Double magnetic fluid	0.12–1.2	[54]
	Roller spinning	1.25–12.5	[55]
Surface type	Sputtering of spinneret	0.44–6	[56]
	Bubble spinning	0.06–0.6	[57]
Clover leaf	Pyramid	2.3–5.7	[58]
	Cone coil	0.86–2.75	[59]
	Spiral coil	2.94–9.42	[60, 61]

fiber fineness, pore feature, and spinnability of the fiber. On the other side in melt electrospinning process, because no solvent is involved, the effect of ambient humidity on the spinning process is not obvious, but when the ambient humidity is too high, excessive voltage loaded will be more likely to cause the air to breakdown [39]. Zhmayev [46] studied the environmental temperature effect on melt electrospinning and found that by increasing the ambient temperature near the nozzle, fiber fineness has significantly changed. Warner [62] pointed out that the temperature of the spinning path will make a big effect on fiber diameter, so he set up a control device for spinning temperature path and depicted the three-dimensional distribution diagram of temperature in different locations of the spinning area. Therefore, in melt electrospinning, in order to prevent the air from the breakdown, high humidity needs to be avoided. In the occasions of high accuracy spinning control requirements, the spinning path needs to be precisely controlled in order to obtain finer fibers.

Indirect melt electrospinning writing process, Liao et al. [63] studied the effect of humidity on melt electrospun polycaprolactone (PCL) scaffolds. In the study, melt electrospun PCL scaffolds were produced with a 90-degree crosshatch architecture at three specific humidity [H_2O/air (g/kg)] levels, low, standard, and elevated, as Fig. 7 shows. Results indicated that humidity does not play a significant role in affecting these scaffold parameters during fabrication. This result shows the environmental stability of melt electrospinning again in comparison with solution electrospinning.

Process Parameters and Fiber Diameter

Melt temperature, spinning distance, applied voltage, and melt feeding rate are important basic parameters of melt electrospinning process. Liu [64] using polypropylene materials with different flow exponents systematically researched on temperature, voltage, distance, and the importance of melt flow index (MFR) effect on the fiber diameter variations, by orthogonal experiment, pointing out that the order of importance was MFR > spinning voltage > spinning distance > melt temperature. Lyons [11] studied melt electrospinning technology, pointing out that with increased electric field, fiber diameter markedly decreased and as the melt feeding rate decreased, both sizes of Taylor cone and fiber diameter decreased. In PLA melt electrospinning experiments conducted by Zhou [47], he found that with higher melt temperature, fiber diameter reduced and fiber diameter distribution became narrower, and with increased electric field strength, fiber diameter decreased but has no big effect as temperature. Ratthapol [39] confirmed this in vacuum melt electrospinning experiments. The conclusion can be drawn that, in melt electrospinning, the system viscosity of the melt is at least an order of magnitude higher than the solution system, so melt viscosity is a vital factor in assessing the spinnability and fiber diameter of a material. With the same distance, increasing voltage and reducing the feeding rate of melt can effectively reduce fiber diameter but require a balance of efficiency and spinning of fiber diameter.

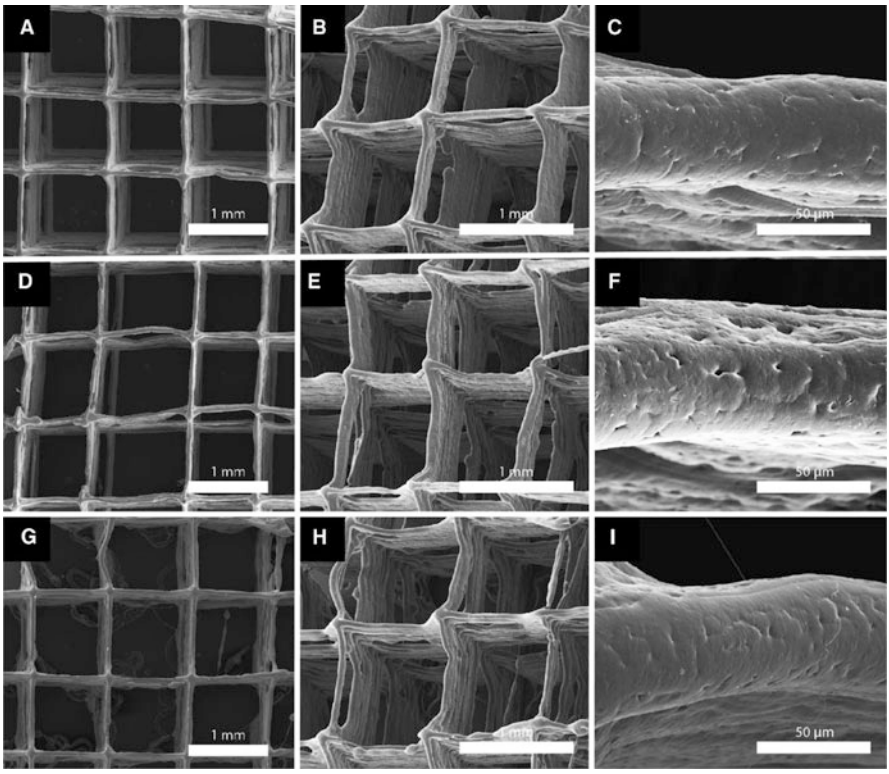

Fig. 7 Representative SEM of each scaffold at different humidity levels. (**a**–**c**) Low humidity, (**d**–**f**) standard humidity, and (**g**–**i**) elevated humidity. No noticeable difference is seen within the imaging parameters of scaffold ordering, fiber diameter, or fiber surface morphology across all groups [63]

Air Auxiliary Parameters and Fiber Refinement

Gas-assisted melt electrospinning has two advantages. First, jets accelerating with air tensile force rub on them resulting in jet thinning. Second, hot airflow controls temperature through the jet path, delaying solidification of fiber, which extends the thinning distance. Zhmayev [46], from Cornell University in the United States, studied the effect of gas assisting on PLA melt electrospinning fiber refining with gas-assisted melt electrospinning device (Fig. 8), finding that air-assisted fibers were 10% thinner than those without a gas stream, and by thermal-assisted electrospinning, it's 20 times thinner. As with the increase in velocity and temperature of the gas, fiber diameter decreases, but a specific trend was not mentioned in the article. In the US Patent US7887311B2 [65], this feature has also been described, but only the specific embodiments of the solution, melt thinning effect, failed to make the embodiment.

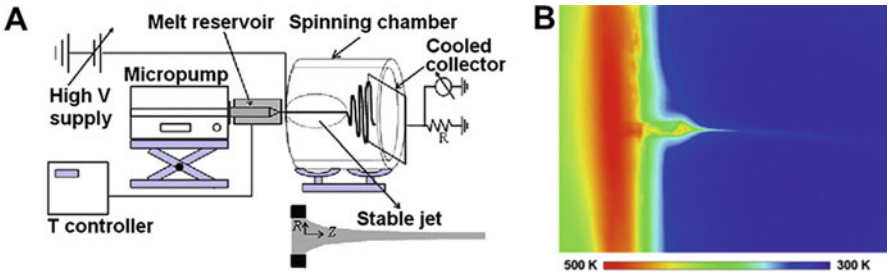

Fig. 8 Gas-assisted melt electrospinning device. (**a**) Schematic of the polymer melt electrospinning setup and (**b**) a thermal image of polylactic acid melt electrospinning without spinning region heating [46]

Material Characteristics and Fibrous Degree of Fineness

Material modification of melt has a great influence on fiber refinement. Ogata [66] developed the carbon dioxide laser-heated melt electrospinning system to electrospun poly(L-lactide) (PLLA), adding poly (ethylene-co-vinyl alcohol) (EVOH) as a coating on PLLA, has a significant effect on decreasing the fiber diameter, that diameter dropped sharply from3 μm down to around 1 μm. Dalton [22] prepared blends of poly(ethylene glycol)-block-poly(ε-caprolactone) (PEG47-b-PCL95) and poly(ε-caprolactone) using the self-made electronic textile machine, finding that the ratio of the components has an impact on fiber diameter. Malakhow [67] used stearic acid and oleic acid as a plasticizer to reduce the viscosity of polyamide 6; by adding 10% of plasticizer, the average diameter of the fibers obtained was reduced by 40 times due to a decrease in the viscosity of the melt by 60 times. Wang [68] added diisooctyl phthalate (DIOP) to poly(methyl methacrylate) (PMMA), and fiber diameter dropped from 34.0 to 19.7 μm. Zhao Fengwen et al. [69] added 8% of stearic acid to polylactic acid (PLA), and the fiber diameter dropped from 5.37 μm down to 1.65 μm. Xia Lingtao et al. [70] added 8% hyperbranched polyester (HBPE) into polypropylene (PP), and fiber diameter dropped from 5–6 μm down to 1–2 μm. Molecular weight is an important factor in melt viscosity of a material. Lyons [71] used polypropylene (PP) with different molecular weight directly to spin polypropylene with an average molecular weight of 580,000, 190,000, 106,000 and 12,000 spun fiber with diameters of 466.15, 10.58, 6.92, and 3.55 μm, respectively. Lyons also found that stereoisomer of polymer structure has a significant effect on the diameter of the fiber. Under the same conditions of spinning, isotactic polypropylene with approximate molecular weight spun the fiber with an average diameter of 3.55 μm, while atactic polypropylene had an average diameter of up to 21.30 μm. Molecular weight can be controlled by adding a different amount of chain-cutting agents. A recent investigation found that by adding 5% (mass fraction) of Irgatec viscosity reducer, the diameter of the fiber will drop from 35.6 ± 1.7 μm to 840 ± 190 nm [38].

The conductivity of polymer melt is a crucial factor in fiber refinement. It has a significant effect on fiber fineness. The solution system has a higher conductivity due to the easier migration of charge to the surface, while most of the melt has less surface charge, which means good dielectric. So the transfer of charge will hardly result in a weak electric field. Thereby, improvement of polymer melt conductivity in order of refining fiber became the focus of the field. Nayak [38] added sodium oleate and NaCl to the low viscosity polypropylene to increase conductivity; as a result, electrical conductivity increased from 10^{-9} to 10^{-6} S/cm, and fiber diameter dropped from 4 μm down to 0.3 μm, eliminating the effect of viscosity.

Laser Assistance and Fiber Refining

In melt electrospinning process, in order to avoid interference between heating electrical control systems and high-voltage electrostatic, the researchers used a variety of heating methods. Laser heating due to advantages, such as concentrated energy, instantaneous melting, and noninterference, is widely used by researchers. Equipment and related researches are classified as laser melt electrospinning [71]. Laser power and the speed of bat material supplied are main parameters for controlling laser melt electrospinning. Voltage diversity has different impacts on diameter from other processes. Takasaki [72] has shown that fiber diameter decreases as the laser output power increases. Ogata et al. [37] showed fiber diameter decreased exponentially as the output power increased, and to a certain extent, fiber diameter remained constant. What needs to be aware of is that if the laser output power is too high, the polymers may decompose, resulting in droplets or beads. In the literature, researchers on voltage effect on fiber diameter obtained different results. The literature [71] showed that the fiber diameter decreases when the voltage decreases. The literature [36, 37] showed that as the voltage increases, fiber diameter decreases exponentially, finally reaching the fixed value. The authors of those articles think it is the disadvantages of laser heating that cause the different results. Due to instant heating of laser, it is unable to monitor the transient state of the melt. Also, fiber diameter is the result of interaction between the electrostatic field and surface tension forces; the uncertainty of the state of melt means the unstable surface tension.

Some researchers conducted preliminary electrospinning experiments using composite melt material. Detta [40] melt electrospun PCL and poly(ethylene glycol)-block-poly(ε-caprolactone) (PEG-b-PCL) composite. PEG-block-PCL has low molecular weight, which is unable to form a continuous fiber. By adding PCL to improve its spinnability, fiber with a diameter of 6–33 μm can be obtained by adjusting the PCL ratio. Li [73] used custom-made platform for a study on PET/SiO_2 blending material and prepared microfiber with a diameter of 500 nm–7 μm. Cong [74] melt electrospun PEG/PVDF composite with core-shell structure, discovering that 42.5% 4000 Da PEG composite material has the latent heat of fusion up to 68 J/g.

Research Progress of Melt Electrospinning Devices

There has been a substantial amount of research carried out on the fundamental aspects of electrospinning technique as a whole. The major issue that is yet to be resolved is the scaling up of the process for commercialization. Solution electrospinning apparatus is simple in its construction. Research groups have constructed the basic electrospinning setups to suit their experimental needs and conditions. Yet studies on melt electrospinning apparatus are still in the early stages, but it is improving. Due to the varying methods of material plasticity, several melt electrospinning devices have been developed, including laser heating [36, 37], electric heating [50], hot air [15] indirect heating, infrared irradiation [39] indirect heating, thermal bath heating [40], and so on. Most researchers use the indirect heating system. Because of the influence of solution electrospinning devices, they tend to put high-voltage electrode on the nozzle or needle. The use of electric heating or another direct heating method can easily lead to the heating of electric circuits or metal components, the breaking down of the high-voltage electrode, and, finally as a result, the termination of the whole spinning process. Aiming to solve the shortage of traditional needle nozzle equipment, Yang's team at Beijing University of Chemical Technology developed a melt differential electrospinning method for preparing ultrafine fiber, smaller than 1 μm in diameter, with a yield of 10–20 g/h. Principle and equipment of melt differential electrospinning will be introduced in this chapter. Several examples of device innovation and inspiration will be described in this section.

Laser Melt Electrospinning Devices

In 2006, Ogata [36, 37, 51], from the University of Fukui in Japan, developed laser-heated melt electrospinning apparatus (Fig. 9). It used to electrospun poly (ethylene-co-vinyl alcohol) (EVAL), poly(lactide) (PLLA), and polyamide 6/12, systematically testing the impact laser power and voltage had on fiber fineness and crystallinity. Polymer (billets or sheets) is rapidly molten and instantly reaches a very low viscosity, and then melt is slenderized by electrostatic force. Through this method, fiber can reach 1 μm in diameter or less. In 2009, Shimada [51] used a linear laser heating device to spin EVOH sheet melt for better spinning efficiency, with a distance of 5 mm between Taylor cones (Fig. 10). In 2011, Li Congju's research group [71] spun different materials using laser melt electrospinning devices. Utilizing its advantages such as instant heating, low-energy consumption, and no interference with high-voltage electrostatic loading system, the laser may serve as a good experimental device, but temperature and viscosity of the polymer cannot be effectively controlled, as well as its high cost and security issue, which is needed to be carefully researched. So this technique is limited on the way to industrialization.

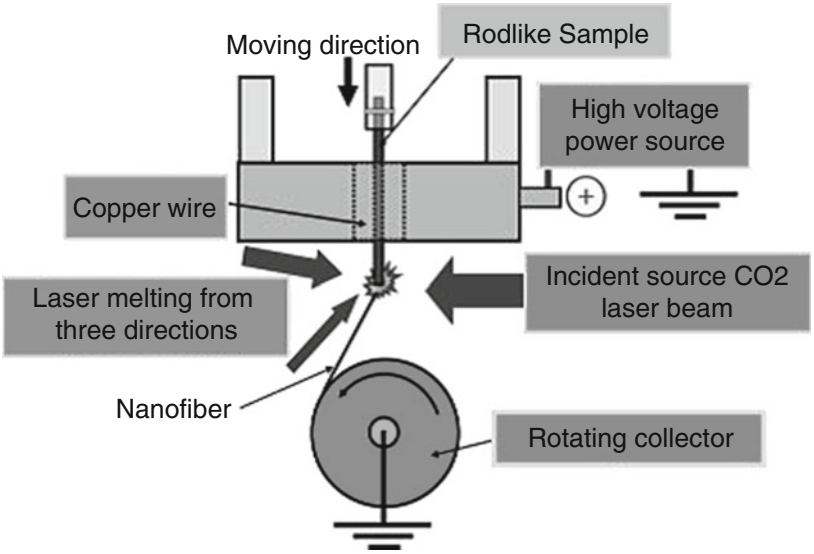

Fig. 9 Schematic diagram of laser melt electrospinning [36]

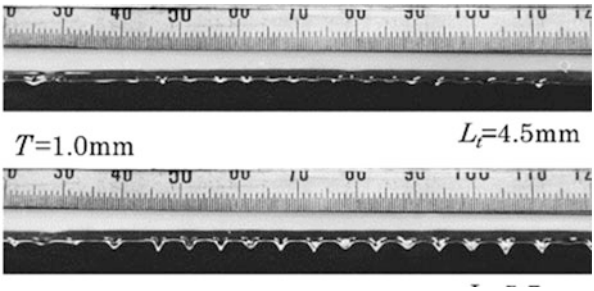

Fig. 10 Multi-Taylor cones of melt electrospun EVOH using linear laser heating device [51]

Screw-Feeding and Narrowly Stitches Melt Electrospinning Devices

Precise control of the temperature and flow of polymer melt is an important key to melt electrospinning devices. Most researchers use microthrusters or air pressure to control the melt feeding velocity precisely. Lyons [11, 13] and Deng [45] adopted the single-screw extruder to the plasticized polymer and control flow. Due to the too large size of the screw, accuracy was not ideal. In order to achieve low flow velocity, they even decreased the screw speed to 0–1 r/min. Some researchers precisely controlled the flow using micro-screw [50]. Erisken [75] tried a twin-screw extruder (Fig. 11), realizing composite online blending and melt electrospinning. Twin-screw extruders were isolated from needles, so electrical interference does not occur. The device adopting the needle, which has a flow rate of only 0.9 mL/h, makes the screw's function not fully used. It is a traditional way of forming plastic melt through

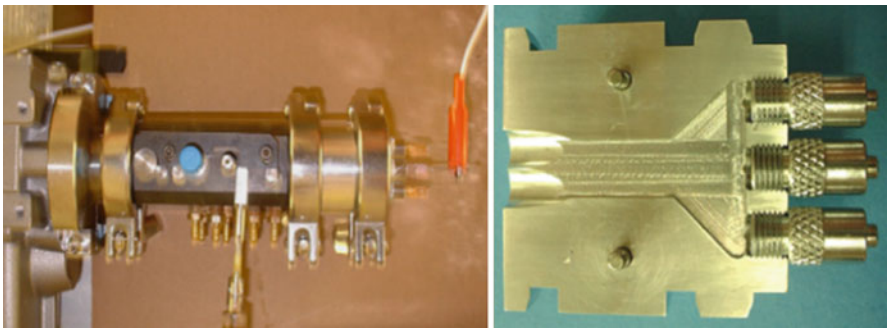

Fig. 11 Micro twin-screw extruder for melt electrospinning and a three-needle die fixed on it (the right photo) [75]

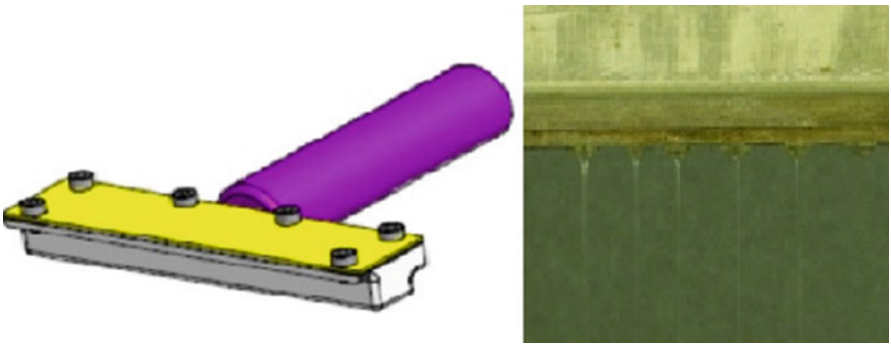

Fig. 12 Sketch and processing picture of the "cleft"-type melt electrospinning [19]

screw realizing control of flow and temperature; choosing the right model combining with the efficient nozzle is an important way to realize industrialization in the future.

Michal Komarek [19], from Technical University of Liberec, Czech Republic, proposed a "cleft"-type melt electrospinning device (Fig. 12), in order to increase the spinning efficiency and avoid needle jams. It was observed that the space of polypropylene jet is 6.3 mm. Materials with lower viscosity had uniform distribution, while materials with higher viscosity had large space between jets and uneven distribution of jets. This method is a desirable choice of needleless melt electrospinning, but tunnels need to be designed in an elaborate way to make flow uniformly distributed.

Disc Melt Electrospinning Devices

Fang J. [18] from Australia, inspired by the electrode inversion method and needleless electrospinning "Nano Spider" invented by the Czechs, proposed a disc

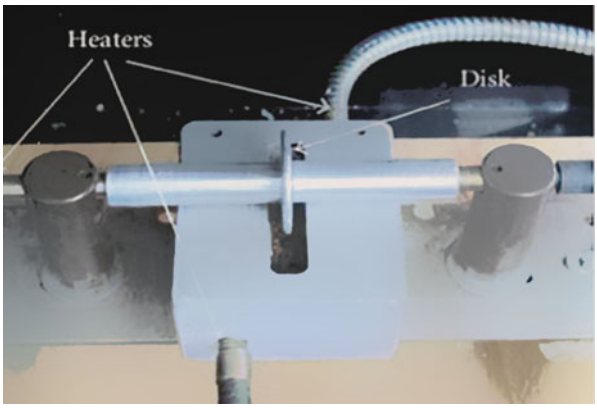

Fig. 13 Photos of the disc melt electrospinning setup [18]

as melt electrospinning device (Fig. 13). The finest fibers produced had an average diameter of 400 ± 290 nm. But the device was able to work only when the melt viscosity was extremely low. Key issues like controllable steady mass production have not been studied yet.

Melt Electrospinning Direct Writing Technique

Farrugia [76] using a 2D motion platform as the collector, through fitting the speed spinning and motion platform, obtained controllable linear-oriented fibers with a 3D structure. As Fig. 14 shows, the polycaprolactone (PCL) was used to electrospun in one embodiment, under the condition of 70 °C, 12 kV spinning voltage, 30 mm spinning distance, and the receiving platform moving speed of 1 m/s. Fibers formed had multi-oriented alignment and diameter varying between 12.5 and 20 μm. It was expected to play an important role in tissue engineering. As early as 2006, Mitchell [77] invented the controllable melt electrospinning devices, in which he also designed indirect collecting platform with structures based on controllable movements in x-y-z directions to realize controllable collecting, but no direct writing feature was proposed. The spinning distance used was 170 mm, which was much longer than the direct writing demand and poor controllability of orientation.

Melt Differential Electrospinning Technique

Melt differential electrospinning (MD-ESP) is a process in which melt flow is self-organized and divided into tens of minor Taylor cones under the stretching force of electric field, and that's why it is named melt differential electrospinning.

Figure 15a, b shows the section view of a typical melt differential electrospinning device. It consisted of five major components: melt inlet, melt distributor,

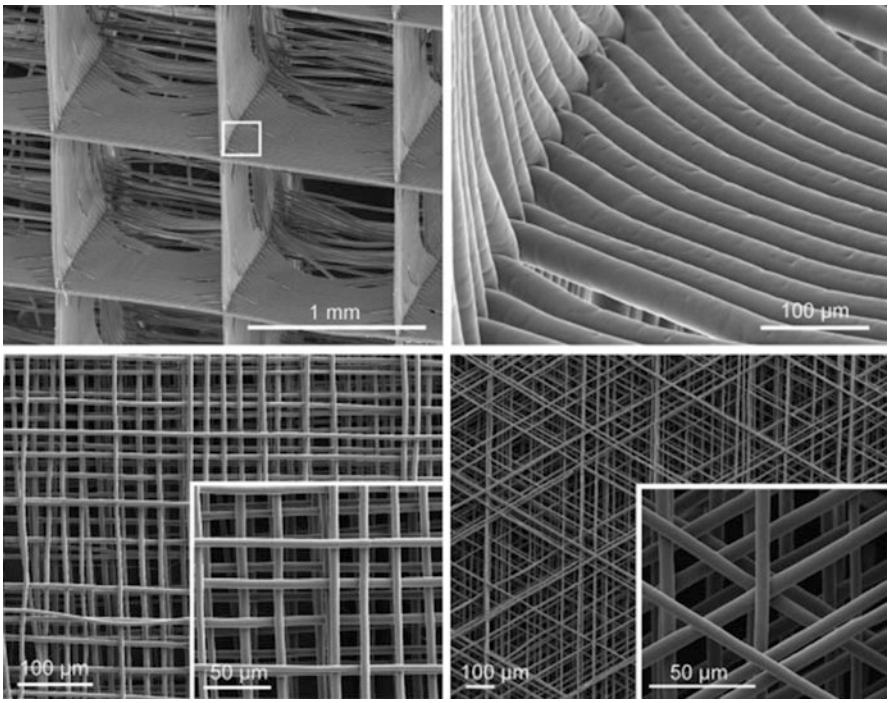

Fig. 14 SEM images of three-dimensional fiber structure produced by melt electrospinning direct writing method [76]

umbellate nozzle, high-voltage power supply, and receiver plate. The processes of this method are shown below. First, melt the polymer, and extrude it forward, and transform it into the uniform ringlike flow. Then, distribute the ringlike flow to the umbellate nozzle with the help of a hot wind. At last, when the voltage surpassed a critical value, multiple jets around the rim of the nozzle were produced and collected to the receiver plate (Fig. 15). It was found that interjet distance of the multiple jets depends on the electric field strength, material properties, and melt viscosity. This process abandons the traditional capillary tube or needle, and realized tens of jets from one small head, and enabled the scaling-up preparation of nanofiber in solventless way. Since now, several thermoplastics including poly (lactic acid) (PLA) and polypropylene (PE) have been processed into nanofiber (Fig. 16).

Emerging Applications of Melt Electrospun Fibers

Micro-/nanofibers produced by melt electrospinning technique have enhanced physicomechanical properties, the fibers have high specific surface area due to their small diameters, highly pores, no surface defects, smooth, and most importantly

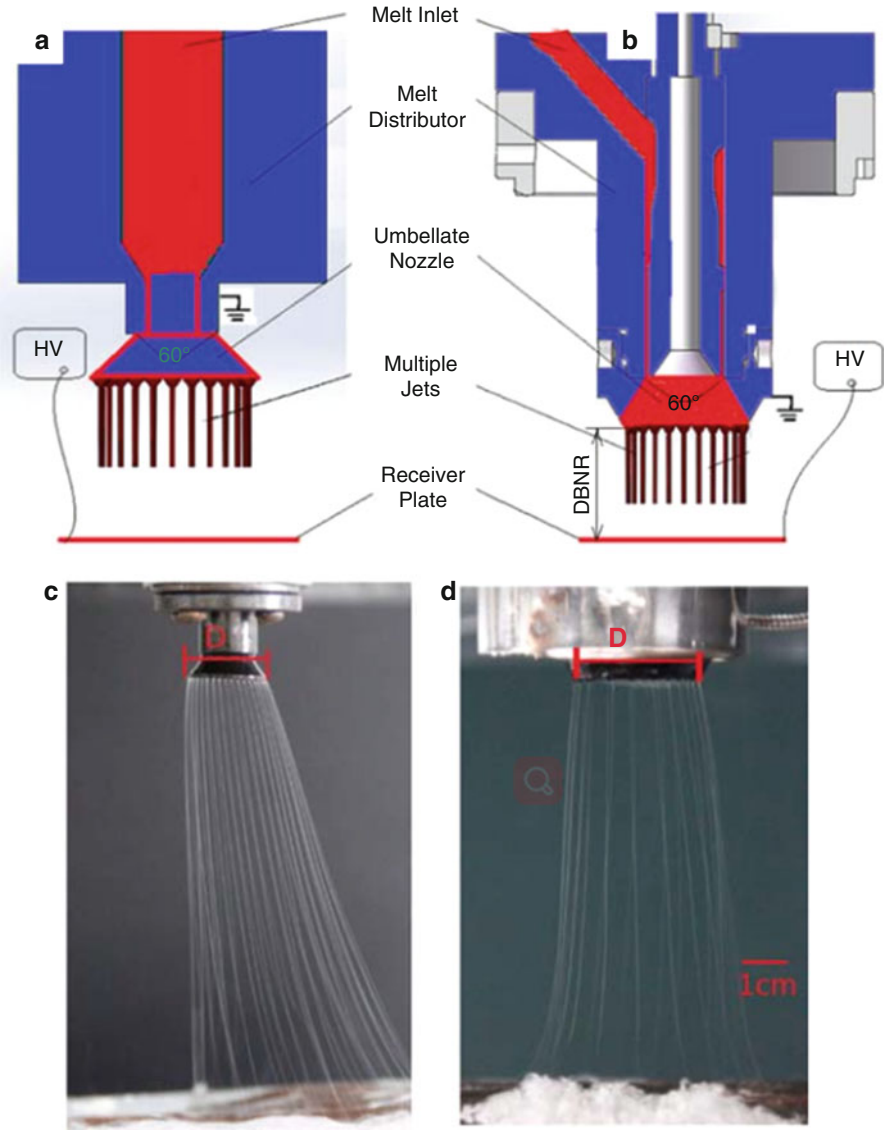

Fig. 15 Melt differential electrospinning applied two types of configurations: (**a**, **c**) nozzle with melt distributed on the outer surface of the umbrella-like nozzle and (**b**, **d**) nozzle with melt distributed on the internal surface of the umbrella-like nozzle [50]

solvent-free. These unique characteristics plus the functionalities of the polymers themselves impart melt electrospun fibers with many desirable properties for advanced applications, such as biomedical, environmental, and energy applications. Highly new applications have been always explored for these fibers continuously.

Fig. 16 Photo of (**a**) the pilot prototype of the polymer melt differential electrospinning device. (**b**) Pilot prototype in running

Fabrication of Nonwoven Fabrics

Solution electrospinning nonwoven fabric layer (nonwoven) has been used to make protective clothing or clothing layer. Due to microlevel diameter, holes between fibers range from several microns to dozens of microns; melt electrospun fibers permit gas passing through freely. Through material modifications or transformation of fiber film as surface features, even superhydrophobicity and superoleophilicity can be achieved. These features can meet the requirements of protective clothing in medical or military fields, as well as be used for developing thin absorbent sportswear.

Facing the contradiction between the high barrier and the high air permeability of traditional protective clothing, Lee [78] experimented basic properties of melt electrospun polypropylene webs and showed that melt electrospun polypropylene webs provided excellent barrier performance against the high surface tension challenge liquid and performance of 90–100% for challenge liquids with varying surface tension, while penetration rate for air reduced by almost 20% which is still higher than most of the materials currently in use for protective clothing. Polyethylene terephthalate (PET) and its recycled plastic are one of the main choices to produce thin and absorbent fabrics in the textile industry. Rajabinejad [79] used particles of recycled PET bottle to melt electrospun; fibers prepared were less than 100nm, which means it could be of a potential use in fields like protective clothing and

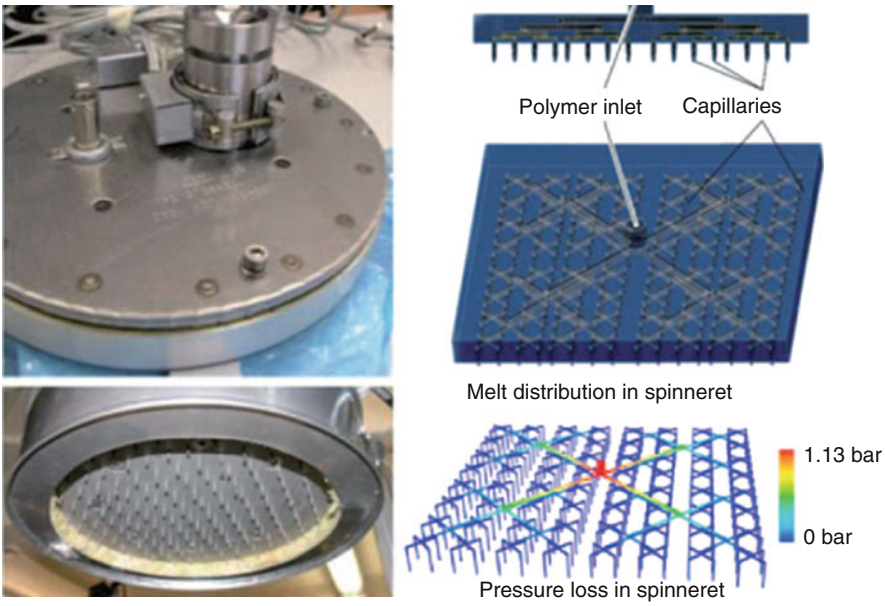

Fig. 17 Multi-nozzle melt electrospinning device [23]

others. Fibers in few micron or submicron level are able to get through the contradiction between the high barrier and the high air permeability of traditional protective clothing; therefore, it is necessary to carry out a series of studies and research work on scaling up melt electrospinning mass production as it is relevant and applicable to the textile manufacturers. Germany RWTH Aachen University research group reported an expanding research outputting through multi-nozzle melt electrospinning device that delivers a polymer melt to a 64-needle array [12] and can make filtration mesh at a rate of 18 m^2/h (Fig. 17) and diameter of 552 ± 260 nm.

Water Treatment and Membrane Filtration

Physical filtration has many advantages like being compact, simple, and environmentally friendly and has been rapidly developed in recent years, especially membrane filtration. Microfiber membrane has stereoscopic micropore structure; therefore, it has a lot of potential applications in water treatment, air filtration, and oil-water separation. Li Shen [80] studied air filtration using PET membranes from melt electrospinning. PET microfiber layer from melt electrospinning with an average diameter of 2.54 μm was attached to the surfaces of the nonwoven substrate with an average fiber diameter of 12.25 μm. Twelve minutes later, the membrane of compound single jet filtrated over 90% of the particles whose size is over 2 μm. Li [81] studied the properties of melt electrospun polypropylene-oriented fibers used in

water filtration, suggesting that combinations of the different orientated fiber membrane had smaller aperture than the random-orientated fiber and had higher efficiency in rejecting the 0.5 μm particles with a diameter of 2.49 ± 0.418 μm and still maintained nearly the same permeate flux as that of the native membrane. The electrospun-oriented fiber membranes also showed good overall mechanical performance.

Contamination of the marine environments by oil has become a specific and serious problem. And the most widely studied organic synthesis oil sorbent material is mainly on high oil-absorbing resin and oil-absorbing cotton microfiber, which are oleophilic and hydrophobic and have super high oil absorption rate and can be repeatedly used [82]. Polypropylene nonwoven fabrics are being widely used currently as oil-absorbing material because of their oleophilic-hydrophobic properties, good oil/water selectivity, high buoyancy, and scalable fabrication. But polypropylene ultrafine fiber cannot be solution electrospun at room temperature, while melt electrospinning technique overcomes this problem.

Research and exploration of melt electrospinning in this area have just begun. Li [83] prepared a series of polypropylene ultrafine fibers fabricated by self-designed apparatus and made melt differential electrospinning device; the resulting polypropylene (PP) fibers showed the maximum oil sorption capacity of 129 g/g and 80 g/g in regard to motor oil and peanut oil, respectively. The oil sorption capacities for these fibers were approximately seven times that of commercial PP nonwoven fabricated by the melt-blown method. In addition, even after seven sorption/desorption cycles, the oil sorption capacity of the PP fibers made by melt differential electrospinning device was still maintained around 80 g/g, and above 97% of oil could be recovered which indicated excellent reusability and recoverability. Results also showed that porosity played a vital role in determining the oil sorption capacities. Melt electrospun nanofibers of biodegradable PLA also showed similar properties [84] (Fig. 18).

Biomedical Applications

Since melt electrospinning is a solvent-free technique, various biomedical researchers have been interested in it. It is an excellent choice for cell cultivation and medical dilution, by eliminating complex solvent mixtures and removal process and simply by ensuring that the environment is safe or performing sterilization reprocessing after simple disinfection. Most melt electrospun fibers are a few microns in diameter, and the pores between fibers range from several microns to dozens. Fibers can be randomly formed or designed to make 3D structures by bonding or mutual support, which is a benefit to cell adhesion, movement, growth, and maturity. Based on the two reasons above, the application researches on melt electrospinning focus on the biomedical field mostly, especially tissue scaffold and wound dressing. In basic aspects of organic cultivation and the tissue scaffold, unlike the solution electrospinning, high-speed jet does not exist in melt electrospinning, which is uncontrollable, but the problem like swing because of low viscosity which

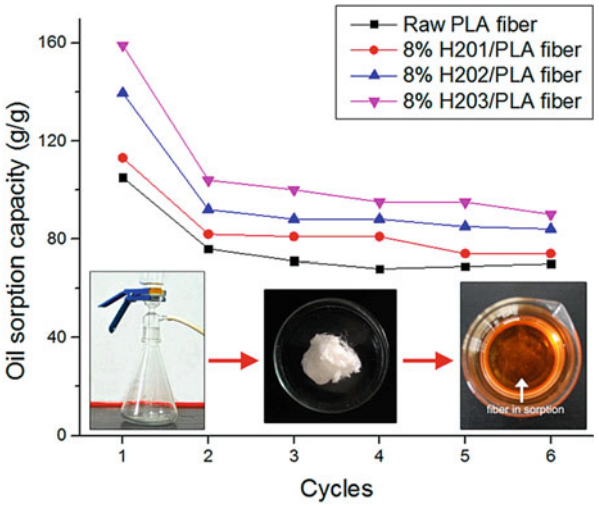

Fig. 18 Oil sorption/desorption cycles of melt electrospun PLA fibers (H201, H202, and H203 are three types of hyperbranched polymers) [84]

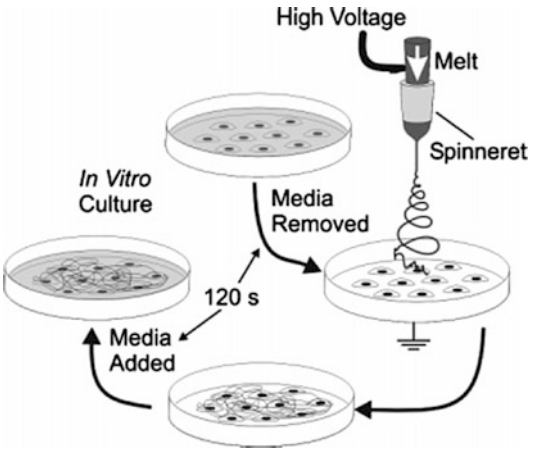

Fig. 19 Process of direct in vitro melt electrospinning [85]

may also result in uncontrollable deposition. Thus, most researchers used direct writing method or direct spinning method, which greatly shortens the spinning distance, only using linear part, generally less than 1–2 cm. There were many recent investigations in this field [85–89]. In 2006, Dalton firstly proposed to melt electrospun directly into cell Petri dish (Fig. 19) or what is known as "direct in vitro electrospinning"; the materials used were a blend of poly(ethylene oxide)-block-poly(ε-caprolactone) (PEO-block-PCL) with PCL, and fibers were prepared with a diameter of 1–2 μm [85]. The cell proliferated, spread, and finally formed a multilayer and separated from the basic. In the year 2008, Dalton [86] published that controllable graphics of melt electrospinning could be used in tissue engineering, and by the x-y controlling speed of the work platform, linear electrospun fibers can

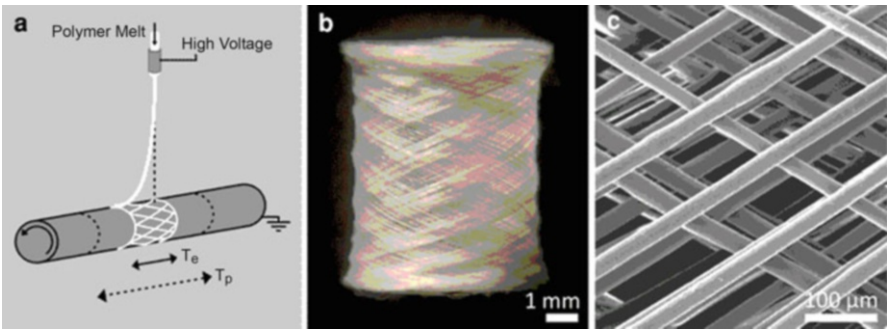

Fig. 20 Porous tube fabricated by combining melt electrospinning with direct writing: (**a**) schematic presentation of the techniques. (**b**) Porous tube of PCL fabricated by melt electrospinning with direct writing; (**c**) SEM image of the obtained fibers, oriented at 60° to the central axis of the tube [87]

be obtained. The main influence to prepare complex graph structures was explored; one of the embodiments showed that the fiber prepared had a diameter of 0.96 ± 0.19 μm and spinning distance could range from 200 to 400 μm. The researchers showed that graphics mainly were controlled by melt flow, voltage, the relative velocity of the jet, and the collector. In 2012, in order to avoid the uncontrollable sediments in solution electrospinning, Toby [87] tried melt electrospinning method using poly(ε-caprolactone) (PCL) to construct three-dimensional controllable-orientated tube scaffolds (Fig. 20) through coordinating speed of rotation and circumference; experimental statistic showed fiber diameter is in the range of 19.9–27.7 μm. Growing experiments of three types of cells showed that cells can penetrate freely between fiber layers and grow well, which lays the foundation of external vessel cultivation. Farrugia [76] also combined melt electrospinning technique with x-y receiving table and prepared poly(ε-caprolactone) (PCL) scaffold using melt electrospinning in a direct writing mode, with fiber diameter of 7.5 ± 1.6 μm, interfiber separation distances ranging from 8 to 133 μm, and an average of 46 ± 22 μm, and the resulting scaffolds had a highly porous nature of 87%. Cells grow well by implanting on the top.

Those studies have shown good controllability of melt electrospinning technique in scaffold printing for the combination of its linear jet parts and 3D work platform and collector; fiber diameter and porosity meet exactly the requirements for cell growth. Therefore, further researches in this field are needed. There are little researches on melt electrospinning used for wound dressings, but it is more easily and quickly to be commercialized. Lee [90] prepared poly(lactic acid) (PLA) micro-/nanofibers using melt electrospinning with a diameter of 1.5 ± 0.8 μm. Comparing melt electrospinning and solution electrospinning (spinning solution/chloroform-acetone (3/1, v/v)), pre-osteoblast cells (MC3T3-E1) were cultured on both solution electrospun fibers and melt electrospun fibers in osteogenic media, and it was found that the BMP-2 and OCN expressions from cells on the melt electrospun fibers were

6-fold and 1.8-fold greater than those on the solution electrospun fibers, respectively. In addition, melt electrospun fibers provided a significantly high cell viability approximately twofold greater than solution electrospun fibers. Hacker [91] did a research on thermoplastic polyurethane (TPU) used in wound dressings, particularly as a porous structured electrospun membrane. TPU was processed into a porous, fibrous network of beadless fibers in the micrometer range (4.89 ± 0.94 μm), and the surface of the fibers was modified with poly(ethylene glycol) (PEG) and silver nanoparticles (nAgs) to improve their wettability and antimicrobial properties; fiber membrane showed favorable antibacterial properties, expected to be new antibacterial and moisture controllable wound dressings.

Conclusion and Future Outlook

Despite the slow progress made in melt electrospinning process, device improvement and control, considerable challenges, but with a deep understanding of researchers and industry to it, the technology is gaining more and more attention. Despite those challenges, melt electrospinning remains an eco-friendly manufacturing method since no solvent is involved, and it has the potential to produce micro-/nanofibers with a smooth and continuous surface, with the need of a new technology very different from solution electrospinning. The authors of this chapter think there are several points worthy of being focused on in the future:

1. The development of basic materials with low molecular weight and low viscosity should be strengthened in order to enhance research and develop industrialization facility. More attention should be given to eco-friendly polymers since most of the electrospun fibers obtained have been synthetic with the aim of achieving fibers with better biocompatibility and performance.
2. Further research on needleless melt electrospinning is needed, on the basis of recognizing characteristics of melt electrospinning; auxiliary air and auxiliary vibration method needs to be added to prepare ultrafine fiber with sub-micrometer and high efficiency. Melt direct writing technology is able to establish the ideal 3D structure through precise control, which attaches great importance to catalysts, sensors, or carrier of the tissue cells. This is the focus of interdisciplinary research.
3. Reasonable design of composite fiber membrane combining several technologies should be researched for applications to achieve high-efficiency filtration with high passing rate and low pressure, making full use of the melt electrospinning fiber layer in composite fibers and membranes.
4. The baggiest challenge is to completely understand the melt electrospinning mechanism. It is necessary to understand quantitatively and carry out melt electrospinning process efficiently, repeatedly, and safely, in the aim to control the properties, orientation, and mass production of the nanofibers.
5. Biomedical applications of melt electrospinning will be increasing and remain in the research literature, due to the nature and speed of commercializing

regenerative medicine and tissue engineering concepts. The potential of scaling up this technology for commercialization, which government agencies, academia, and industry should pay attention to, is an important issue for further growth and development of the field. In the future, melt electrospun nanofibers will prove to be a promising candidate for a wider range of advanced applications.

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