Principle and equipment of polymer melt differential electrospinning preparing ultrafine fiber

Yang Weimin1,2, Li Haoyi1,2,

1College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing 100029, China
2State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

E-mail: yangwm@mail.buct.edu.cn

Abstract: Two methods preparing polymer ultrafine fiber have been developed: solution electrospinning and melt electrospinning, among which, solution electrospinning is much simpler to realize in laboratory or industry. More than 100 institutions have made endeavors to research it and more than 30 thousand papers have been published. However, its industrialization was restricted in some extent because of existence of toxic solvent and low strength caused by small pores. Solventless melt electrospinning is environment friendly, but high melt viscosity, thick fiber diameter, low yield and complex equipment lead to less research on it. Aiming to solving the shortage of traditional needle nozzle equipment, we first proposed a melt differential electrospinning method preparing ultrafine fiber, through which fiber smaller than 1 micrometer can be produced and a yield of 10-20g/h can be achieved by a needleless nozzle. Further more, principle and equipment of melt differential electrospinning are introduced.

Key words: melt electrospinning; differential equipment; needleless nozzle; fiber

1. Introduction

Reneker's[1] research work on electrospinning showed sound prospects for artificial nano-fiber preparation, which set the world on the research upsurge of polymer electrospinning in the past twenty years. As shown in figure1, on recent ten years the development of electrospinning research shows that number of published papers on solution electrospinning is nearly a hundred times that on melt electrospinning. The main reason lies behind this huge contrast is that the solution electrospinning experiment device is much simpler[2] while the melt electrospinning is relatively complex[3]. However, evaporation of solvent in solution electrospinning may cause small pores on the fibers[4] and environmental pollution[5], at the same time, polypropylene, polyethylene and some other materials have not found a suitable solvent at room temperature[6]. These facts limited the industrialized application of solution electrospinning technology. Now it is urgent to solve the bottleneck problem of melt electrospinning and realize green manufacturing technology of ultrafine fiber in industry.
In 1936, Charles Norton’s patent[7] showed the earliest description of melt electrospinning and solution electrospinning. However, half a century later, in 1981, the first scientific literature on melt electrospinning was just published[8]. After 20 years, the second article on melt electrospinning published by Reneker and Rangkupan [9] introduced the PP, PE, PET, PEN melt electrospinning in vacuum. In the last 10 years, more than 30 papers on melt electrospinning has been published. Representative results are as follows: Nobuo Ogata team of Fukui University [10] developed a laser heating melt electrospinning, they made the polymer bar heated and molten by laser, then electrospun fibers within 1μm; Jason Michael Lyons[11] and Cevat Erisken [12]tried melt electrospinning using single screw extruder and twin screw extruder respectively. Complex designing was involved in these devices to avoid electrical interference.

In order to elevate the electrospinning production, most researches focused on increasing the quantity of spinning needles. A multi-needle melt electrospinning equipment was produced by ITA Aachen of Germany as shown in figure 2 [13], however, the simple combination of fine needles was of low efficiency, high cost and complex hot runner. With the development of needleless technology in solution electrospinning, some needleless melt electrospinning device came to be published. Line-laser melt electrospinning proposed by the Ogata team[14] was an important evolution of laser melt electrospinning. They chose a 100×150mm sheet with thickness of 0.5 to 1 mm. When it was heated by a linear laser, a plurality of Taylor cone will formed at the edge of the sheets. It was 4cm to 6cm between the two Taylor cone (interjet distance), but sometimes Taylor cone may disappear because of un-uniformed spinning parameters. Finally the P(EVAL) and Nylon 6/12 fibers with diameter of 800 nm to 2.5 μm were produced at different parameters (voltage, flow velocity, and laser intensity). Komarek M and Martinova L[15] from Liberec University of science and technology in Czech, proposed a slit-type melt electrospinning device, but how to distribute melt uniformly in the slit remained a problem. Fang J et al[16] from Australia proposed a disc melt electrospinning device, but the device had high requirement of melt viscosity. In conclusion, breakthrough in melt electrospinning technology research may happen only when researches focused on the equipment innovation.
2. The principle of polymer melt differential electrospinning

To develop polymer melt electrospinning technology, three problems should be considered: high voltage insulation and security issues of electrospinning system, fiber refinement, and productivity.

The high voltage insulation and security issues of electrospinning system brought many researchers various problems in device designing. Influenced by traditional solution electrospinning, majority of melt electrospinning experiments were proceeded with receiver plate grounded and the high voltage connected to capillary end. This may cause fire and since high insulated unites were involved. Actually the solution is easy: just to connect the positive high voltage electrostatic supplier to the spinning receiver plate directly, and ground the plasticizing system[17]. As Gaoqi L’s comments[18], this Solution eliminated the obstacle of melt electrospinning to industry.

Melt electrospinning are nearly impossible to prepare nano-scale fiber in mass production using traditional needle-like nozzles, however, the author proposed a principle of melt differential electrospinning: first, the polymer melt was transformed from a cylindrical flow into a uniform ring-like flow, next, the ring-like flow was distributed to the umbellate nozzle, then a thin and uniform melt film formed on the umbellate circumferential surface, finally, when the applied high voltage surpassed a critical value, self-organized multiple jets around the rim of the umbellate nozzle were ejected to the receiver plate spontaneously(figure 3). Interjet distance (figure 4) depends on the electric field strength, material properties and melt viscosity. This process is similar to the so-called “Needleless electrospinning” in solution electrospinning[19], which abandons the traditional capillary tube or needle, applying a higher electric field to the free surface of the liquid to realize multijet self-organization.

As shown in figure 3, a typical melt differential electrospinning device consisted of five major components: melt inlet, melt distributor, umbellate nozzle, high voltage power supply, and receiver plate. Polymer melt was metered and supplied into melt inlet by a self-designed micro extruder, and the melt flow rate could be controlled in the range of 1 – 100 g/h. Melt distributor was designed to induce the single melt flow to the circumference of the umbellate nozzle uniformly. The nozzle was earthed and high positive voltage was loaded on the receiver plate using a high voltage power supply source at a value range of 0–80 kV. Receiver plate was a circular copper plate with diameter of 150 mm and thickness of 3 mm.

![Figure 3. Structure diagram of the two melt differential nozzles.](image)

Based on previous experimental study, it was found that in melt differential electrospinning, polymer melt feed rate had no evident influence on interjet distance. The main factors influencing the interjet distance were electric field strength and polymer melts viscosity. With the field strength increasing at a fixed melt feed rate, the self-organizing differential effect became stronger. It means
that the constant volume of melt supply can be divided into tens of micro flows, thus more jets formed and then solidified. Without the consideration of thinning effect of electric field intensity on fiber diameter, smaller fiber diameter will be attained with the jets number increasing. Assuming melt flow rate is \( Q \) and the resultant single fiber diameter is \( D \), after melt differential electrospinning process, the jet number increases to \( K \), and fiber diameter will become \( D/K^{\frac{1}{2}} \).

Experimental results show that, for a polymer, the lower the melt viscosity or the higher the electric field strength, the shorter the interjet distance. Present experimental study shows that melt differential electrospinning can achieve the minimum interjet distance of 1.1mm (spinning parameters: applied voltage is 35kV, spinning distance is 70mm, nozzle temperature is 260 °C, and spinning materials is Polypropylene), which is only less one third of that by needleless solution electrospinning from free surface (spinning parameters: applied voltage is 43kV, spinning distance is 80mm, and spinning material is the 4% polyvinyl alcohol in water). This result indicates a promising production.

3. The pilot line of polymer melt differential electrospinning

Based on the principle of polymer melt differential electrospinning, a prototype equipment of pilot line was designed and operated. This machine can realize mass production of polymer nanofiber by melt electrospinning route. As shown in figure 5, the equipment includes nine components: a small twin screw extruder, a melt filter, a melt metering pump, a melt differential electrospinning box, air auxiliary equipment, suction device, a lapping machine, and rolling-coiling machine. The melt differential electrospinning(MD-ESP) process and resultant fiber diagram were compared with that of solution electrospinning(S-ESP) in figure 6.

The performance parameter of pilot line are as follows:
Integration of the 32 differential nozzles;
- The jets number ejected from each nozzle (diameter of 26mm) can range from 50 to 100;
- The defined width is 0.8m, output is 300-600g/h, and the average fiber diameter is 500-800nm;
- The thickness of non-woven fabrics is adjustable from 10μm to 1000μm;
- Continuous supply of polymer melt or polymer blend melt can be realized on line;
- Modularly extendable to the 6kg/h production line.

Figure 6. The spinning process of pilot line and the fiber diagram comparison.

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