Research Process of Polymer Nanofibers Prepared by Melt Spinning

Zou Wei
College of Mechatronic Engineering, Jiangsu Normal University, Xuzhou, Jiangsu 221116, China

Abstract. Over the past decade, due to the unique advantages of polymer nano-materials, applications of polymer nanofibers including tissue engineering, protective clothing, filters and sensors has increased significantly. How to prepare polymer nanofibers has become a hot research topic. This paper reviews the process for the preparation of polymer nanofibers via melt spinning developed in recent years, and outlines the advantages and disadvantages of these types of preparation. Finally, development of preparation for the polymer nanofibers has been summarized.

1. Introduction
Polymer nanofibers have the advantages of large specific surface area, small size effect (some new effects in the aspects of physical properties, such as photothermal, electroacoustic, magnetic, etc.), surface and interface effect (large surface activity), quantum size effect, quantum tunneling effect, better mechanical energy [1] and so on, so they are widely used in many fields including environmental protection (high performance filtration membrane), energy (battery), medicine (wound dressing, human tissue engineering, etc.), electronic (sensor), textile engineering, aerospace and composite materials. In order to solve this demand, how to prepare polymer nanofibers has become a research hotspot.

Nanofibers generally mean that the diameter of the fibers is nanoscale and the size is less than 100nm [1] in most cases, the diameter of fibers is less than 1000nm. Traditionally, fibers with diameters below 500 nm are called nanofibers [2] [3].

According to the different state of polymer in spinning, the preparation process of polymer nanofibers can be categorized into melt spinning, solution spinning and emulsion spinning [5] [6]. Based on the specific process, melt spinning is divided into melt electrospinning, centrifugal melt spinning and molding melt extrusion spinning.

2. Melt Electrospinning
Electrospinning, especially solution electrospinning, is a relatively mature process for preparing nanofibers, which has been put into practical production. In the 30s of last century, some people proposed to spin the polymer melt or solution by electrostatics, and Taylor carried out the research on related electrospinning [7]. The principle of this process is based on the effect of electrostatic force on the liquid force, that is, when a suitable charged material is brought to the droplet in the capillary, if the charge density is very high, the droplet forms a conical shape and a small jet will occur at the tip of the small cone, and the middle diameter of the injection process reaches the nanoscale fiber. The fiber was collected by the collecting device and finally obtained nanofibers. The principle is shown in Figure 1. The diameter of the nanofibers prepared by this method is as low as 29nm. According to the different
state of polymer in spinning process, electrospinning can be divided into two categories, namely melt electrospinning and solution electrospinning [5] [6].

Some researchers have proposed the use of polymer melt electrostatic spinning to prepare nanofiber [10] because there are some drawbacks including toxic solvent and complex solvent recovery process in solution electrospinning. Melt electrospinning includes melt feeding devices and other devices similar to electrospinning of solutions, as shown in Figure 2. This process uses different heating devices such as electric heating, heating furnace heating, heat gun, laser heating device and other [4]. According to the different heating methods, it can be divided into electro thermal melt electrospinning, coaxial melt electrospinning, hot gun melt electrospinning and laser heating melt electrospinning.

The quality of melt electrospinning is affected by many important factors such as the nozzle size, the temperature of the spinneret and the die zone, the molecular weight of the polymer melt, the shear and tensile viscosity and the flow rate of the polymer [12]. The diameter of melt electrospinning can reach 1-30 microns, containing 247-500 of nano fiber [13].

There are several advantages of melt electrostatic spinning such as no toxic solvent, high productivity, high utilization of material, easy to get polymer melt blends and suitable for most polymers (such as PE, PP and PET) [11]; but it has many disadvantages [4]: need high temperature melting system, difficult to removal electrostatic, low conductivity, hard to fabricate nanofibers (due to high viscosity and fast curing). Based on the above characteristics, melt electrospinning is still in the laboratory stage.
3. Melt blown spinning
The American naval laboratory took the lead in the study of melt blown spinning. The principle of melt blown spinning is that the melt is extruded from the hole in the mold, the fiber is blown out of the hole and fabricated by air in the hole, and then is collected by a suitable collector to form the fabric. The average diameter of fibers is mainly determined by blowing rate, melt viscosity, air temperature, melt temperature and air flow rate [15][16][17]. At present, nanofibers with a diameter of 50-2000nm [18][19] can be prepared by this process. The productivity of PE, PP, PLA, PS, PET, PU, PVC and PVA nanofibers is about 0.01g/min [20][21]. Hills Company has begun to produce polymer nanofibers with an average diameter of about 250nm, and MFI of this nanofibers is 1500-1800 [22]. The principle diagram and the object of the process are shown in Figure 3.

There are several advantages of melt blown spinning such as no solvent in the preparation process, a wide range of materials especially preparing polymer fibers that cannot be prepared by electrospinning, high production efficiency which is several orders of magnitude higher than that of electrostatic spinning. Due to various factors, the process has the following deficiencies: A. the process is not flexible enough, and needs dies, so each preparation of a diameter of nanofibers should be replaced with a die; B. the diameter of the nanofibers prepared by melt blown spinning is larger than that of the electrospinning, which is mainly restricted by the fabrication technology especially the pore size of the die; C. The degradation may occur during the preparation of nanofibers, which is mainly due to the heating in the preparation process. If the temperature is not properly controlled, the polymer can be degraded; D. The process is more complex, and the temperature and the force of the hot air to the fiber should be controlled reasonably.

![Figure 3. Device and schematic of melt blowing [23]](image)

4. Melt centrifugal spinning
Centrifugal spinning is that the solution or melt of a polymer (or other material), with the help of centrifugal force, is throw out through a small hole in a rotating container to form nanofiber, and the principle is shown in Figure 4. This method, compared with the traditional electrospinning, has increased the production efficiency, and the production efficiency of the latest centrifugal spinning has reached more than 2000 times (1g/min [23] per hole) than that of electrospinning. It has high spinning efficiency, low cost and environmental protection, and can also be used to prepare metal, ceramic and composite fiber other than polymer fiber.
According to the different state of materials used in centrifugal spinning, it can be divided into two main categories: solution spinning and melt spinning. The solution centrifugal spinning is divided into centrifugal electrospinning and pure centrifugal spinning based on whether or not static electricity is used. Generally, if there is no special description, pure centrifugal spinning is called solution centrifugal spinning, also called centrifugal spinning (Rotary Jet-spinning (RJS) or Forcespinning) or high speed spinning.

JP Hooper's patent "Centrifugal Spinneret [24]" proposed the method of preparing artificial fibers by centrifugal force. But the fiber diameter was larger because of condition limitation. This method can effectively produce fiber and fiber rope, but there is a disadvantage of fiber instability. The American patent "Centrifugal Spinning Device [25]" improves the centrifugal spinning to improve the stability of the fiber, but the diameter of the fiber is still above the micron grade.

In order to meet the market demand for nanofibers, many researchers at home and abroad have carried out research on [26] [27] [28] based on the principle of centrifugal spinning. Huang [29] invented the centrifugal spinning nanofiber method, which is applied and put into practical application by the DuPont Co.. The fiber produced by this method is less than 1 μm.

Karen Lozano [30] of Texas University has put forward another centrifugal spinning device and manufactured prototype equipment. The device is equipped with a heating and cooling system. It can not only realize solution spinning but also melt spinning, and can produce polymer, metal material or other composite material fiber. The average diameter of PEO fiber and PAN fiber, prepared by this method, is 300nm and 500nm-800nm, respectively. The production efficiency is more than 1g/min per hole.

The Ed Peno [31] patent for the preparation of nanofiber or micro fiber spinning device was approved and transferred to the enterprise FiboRio Technology Corperation, and the company has produced a series of laboratory grade products, the nanofibers produced by the device can reach the minimum of 45nm, thus it is possible to make the centrifugal spinning into industrialization.

Because of the disadvantages of the solution centrifugal spinning, which requires the use of solvent and is unfriendly to the environment, the solvent recovery process is complex, and the polymer is easily dissolved in a solvent, it is difficult to manufacture high performance nanofibers. But nanofibers are usually widely applied in thermal chemical filtration fields or in lightweight composite materials used in the aerospace and defense fields. Therefore, it is necessary to develop a new way to prepare nanofibers. It is melt centrifugal spinning, in which.

Spinning materials is in melt state. Melt centrifugal spinning is a process in which polymer or other substances melt under the action of centrifugal force, which is thrown from the container of molten storage and finally cooled to form fibers.

The preparation of nanofibers by melt spinning is less than that of solution spinning because most polymer may be degraded at high temperature, the viscosity of the material is larger and the flow property is poor in the melt state, in addition, the cooling and collecting of fiber is a difficult problem to be overcome, and the heat device is required in this process. Asao Oya [32] and others invented a device for preparing carbon nanofibers using the melt with the centrifugal force. The micrometer fiber of tendon sheath structure can be firstly prepared with the melt by this device taking advantage of the centrifugal force to, then heated to form nano scale (diameter 20-50nm, length 200-500nm) carbon nanotubes.
Zhang Pieria [28] et al. invented a device for preparing non-woven fabrics by centrifugal spinning of polymer melts. It was proposed to use infrared heating device to heat or heat polymer melts. Tao Huang [33] et al. invented a high speed rotating disk to prepare nanofibers by centrifugal force. The diameter of the nanofibers was less than 1000nm, as shown in Figure 5.

Karen Lozano [30] et al invented a melt spinning device which can be used to prepare nanofibers of polymers, metals or composite materials. The diameter of the nanofibers is at the micro and nano scale. Zhang Yiqun [34] and other invented "horizontal disc rotating centrifugal spinning". The invention is suitable for the preparation of polymers and various inorganic fibers, but the diameter of the fiber is in the micron scale (1-1000 microns). Zhang Yiqun [35] and other proposed a patent named "electromagnetic heating device and the application of the device's horizontal disc rotary centrifugal spinning equipment". Fibers, prepared by the horizontal disk centrifugal spinning, have better orientation and better performance. Yang Weimin [36] et al. invented a device for the preparation of nanofibers by differential shunt centrifugal spinning. By the design of the conical surface on the rotating structure, the melt in the rotating structure became thinner and uniform under the action of centrifugal force, and the nanoscale fiber was prepared. Liu Yong [37] et al. invented a centrifugal melt electrostatic spinning device. The device makes use of the joint action of high pressure electric field force and high speed centrifugal force to prepare nanoscale microfiber. By adding materials to the feeding room, the continuous spinning can be realized, and the spinning efficiency can be improved and a certain width fiber membrane can be obtained by using the multi-layer nozzle. but the device needs to use the high voltage electric field, which not only increases the complexity of the system and causes certain hazards to the operator, but also limits the use of materials which are required a certain conductivity. At present, melt spinning is at the initial stage of laboratory and industrial application.

5. Template melt extrusion spinning
The process combines the melt extrusion and template method. First, an extruder is used to squeeze a certain amount of melt into the mold (one of the templates contains a certain amount of additive, which is contained in the melt), and the melt in the mold is cooled in the anodic aluminum oxide film hole of the template under the press. After forming, the template containing the polymer is put into the ethanol. The fiber with a diameter of 150-400 nanometers is obtained by ultrasonic [38]. The specific principle is shown in figure 6. Although nanofibers can be obtained in this process, the maximum length of the fiber is determined by the thickness of the template, and the fiber diameter depends on the that of the template hole. Currently, this process is only in the laboratory study stage.
6. Conclusion

Compared with ordinary fibers, nanofibers have many advantages and have wide application prospects in many fields. In this paper, the current status and recent progress of polymer nanofiber spinning process are reviewed. The current status and characteristics of melt electrostatic spinning, centrifugal melt spinning, melt blowing and template melt extrusion are reviewed.

Although there are some problems in melt spinning such as large melt viscosity, poor fluidity and need for temperature control technology, the melt spinning overcame the defects of solution spinning and emulsion spinning. Especially, the melt centrifuge spinning has many advantages such as the environment friendly, simple equipment, solvent free treatment process, no high pressure, wide range of applications (polymers, metals and inorganic materials, etc.), high production efficiency, preparing high performance fibers with specific physical and chemical properties and direct preparation of nanofibrous membranes. If the technical difficulties of melt spinning can be solved in the future, the nanofibers prepared by melt spinning will be better developed and applied in the next few years.

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