Study on the properties of electrospun fiber for wound healing

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Abstract. Electrospinning is a kind of technology which can efficiently prepare wound healing materials. In the application process of materials, it is very important to study the biological and mechanical properties of fiber materials. In this paper, Polycaprolactone fiber was prepared by controlling the process parameters of electrospinning process. The surface structure of the fiber was observed by scanning electron microscope and atomic force microscope. The results of electron microscope showed that there were cross stripes on the fiber surface, which would affect the mechanical properties of the fiber. The mechanical properties of fiber under two kinds of deformation conditions were measured by using high precision drawing equipment and self-made bending device. The experimental data show that the elastic modulus of the fiber under tensile load presents discrete distribution characteristics, and the elastic modulus of the fiber has nothing to do with the diameter; while in the bending experiment, the elastic modulus of the fiber increases significantly with the decrease of the fiber diameter, and the mechanical properties of the fiber show scale effect related to the fiber diameter. The reason for the different mechanical properties of the two groups of fibers may be related to the crystal morphology of the fiber surface and interior.

1. Introduction

Electrospinning is an important method for the preparation of fiber materials developed from melt spinning. The main principle is to use the electric field force to make the polymer solution or molten body form a tip jet, and then form a liquid like thin flow. The polymer solution at the needle overcomes the surface tension and gravity, and ejects along the direction of the electric field into a thin filament. Under the action of the electric field, it further stretched and deposited on the collection device with the solvent volatilization. The process is shown in Figure 1 [1-3]. The fiber film with random distribution can be obtained by flat collecting device, and the fiber aggregate with orientation distribution can be obtained by collecting roller with rotating device [4].

The advantage of electrospinning process is that continuous and uniform diameter fibers can be prepared, and the fiber film with high porosity can be obtained [3]. By adjusting the process parameters of electrospinning, such as spinning temperature, humidity, electric field strength, jet size, type and concentration of solution and solvent, ultrafine spinning films with different fiber diameter, surface morphology and porosity can be obtained. Electrospun fibers have been widely used in biomedical, environmental filtering and industrial protection [5,6].
Polycaprolactone (PCL) is a kind of biodegradable polymer material with good biocompatibility and nontoxicity. Its melting point is 59-64 °C and glass transition temperature is -60 °C. PCL has long molecular chain, hydrophobic groups and slow degradation rate, which can be used for bone tissue repair in tissue engineering [7-9]. PCL has good permeability to small molecule drugs, so it is widely used in the field of drug release [10]. At present, the main research work mainly focuses on the biological properties and degradability of PCL, while the research on its mechanical properties is relatively less. Because the diameter of electrospun fiber is in nano scale, the existing mechanical models have limitations in analyzing and calculating the mechanical properties of nano scale materials, and the experimental test of its mechanical properties is also very difficult [11, 12].

In this paper, PCL micro nanofibers were prepared by electrospinning method, and the surface morphology characteristics of the fibers were characterized and analyzed. The mechanical properties of PCL fibers under two kinds of deformation conditions were analyzed by tensile equipment and bending experimental equipment, and the mechanical properties of PCL fibers under two kinds of deformation conditions were analyzed. It is hoped that the research on the morphology characteristics and mechanical properties of PCL fibers can provide reference for PCL Fiber materials in the process of practical application of structural design to provide a certain research reference.

2. Experimental part

2.1. Materials
PCL (molecular weight about 80000) was purchased from Aldrich company. Solvent: Dichloromethyl (DCM), purchased from Fisher Scientific. N, N-dimethylformamide, purchased from Merck.

2.2. Main instruments and equipment
Electrospinning equipment, self-made. High precision tensile testing machine, NanoUTM, purchased from MTS company. Self made clamping equipment for tensile test. AFM, model: Nanoscope IIIa, purchased from digital instruments company. Bending experiment groove device, self-made. Scanning electron microscope (JSM-5500), purchased from JEOL company.

2.3. Sample preparation
Two different concentrations of PCL solutions were prepared with mass fraction of 10 wt% and 14 wt%. The solvent was dichloromethane and dimethylformamide in the ratio of 4:1 (W/W), mixed and
stirred for 24 hours. The ambient temperature of electrospinning is controlled at 25-30 °C, the humidity is controlled below 50%, and the voltage is set at 15 kV. The electrospinning device is used to prepare fibers. The two ends of the electrode are respectively connected with the syringe needle and the metal fiber collection platform. An electric field is formed between the needle and the metal platform. With the advance of the micro syringe, the polymer solution is extruded from the needle, and under the action of the electric field, the fibers are formed and deposited on the collection device.

2.3.1. Tensile specimen. The specimen for tensile test is prepared as follows. Firstly, a frame for collecting single fiber is made, and the frame is placed on the fiber collection platform. With the electrospinning process, some fibers will settle at both ends of the frame. The specific position of the fiber can be observed by irradiating with a strong light source, and then the single fiber can be transferred to the clamping device for fiber tensile test as shown in Figure 2. The device is composed of the left part of the plastic frame and the right part of the mica sheet. The electrospinning solvent will fix the two ends of the fiber on both ends of the frame. The fiber on the frame is used for tensile test, while the part on the mica sheet at the right end of the clamping device is used to measure the diameter of the fiber [13]. The device can accurately measure the diameter of the fiber while measuring the tensile mechanical properties of the fiber.

![Figure 2. Single PCL fiber clamping device.](image)

2.3.2. Bending specimen. After photolithography, grooves with a certain width are produced on the surface of the silicon wafer, and the width of the grooves varies from 4 to 6 microns. In the electrospinning process, some fibers will settle on the silicon wafer, and the fibers settled on both ends of the silicon wafer groove are selected as the bending test samples.

2.4. Test and characterization

2.4.1. Tensile test process. In the tensile test, firstly, the fiber sample is clamped on the high-precision tensile testing machine. Observe the position of the fiber on the frame with strong light, and adjust the fiber clamping device to make the arrangement direction of the fiber consistent with the drawing direction. Cut off the edge protection of the plastic frame on the left side of the clamping device in Figure 2, and start to load the fiber. The tensile test will record the stress curve of the fiber during the tensile process. At the same time, the fiber on the mica on the right side of Figure 2 will be observed in the atomic force microscope, and the fiber diameter will be measured. According to the force curve and fiber diameter data of the fiber in the tensile process, the tensile mechanical properties of the fiber can be calculated. In order to keep the deformation of the fiber in the elastic range, it is necessary to control the maximum strain less than 0.1.

2.4.2. Bending experiment process. The bending experiment was carried out by atomic force microscope. In the process of electrospinning, the existence of solvent will make the fiber sticky, and the fiber will form a fixed constraint on both sides of the groove after contacting with the groove on the silicon wafer. Therefore, the fiber deposited on the silicon wafer groove can be regarded as a fixed
beam at both ends. The probe of atomic force microscope is used to load the middle position of the fiber, and the deformation of the middle position of the fiber is measured. Then, the bending mechanical properties of the fiber can be calculated by the three-point bending experimental principle as shown in Figure 3. The probe used in AFM is ORT-8, and its elastic coefficient is 0.15 [14].

![Figure 3. Schematic diagram of three point bending test for PCL fiber](image)

The elastic modulus of fiber in three-point bending test can be calculated according to formula (1)

\[ E = \frac{PL^3}{192vI} \]  

(1)

Where \( P \) is the maximum load exerted by the AFM probe on the middle position of the fiber, \( L \) is the length of the fiber at both ends of the groove, \( \nu \) is the deformation of the fiber center, and \( I \) is the moment of inertia.

Figure 4 shows the relationship between the cantilever offset \( D \) of the probe and the displacement \( Z \) of the piezoelectric sensor during the fiber bending experiment. The dotted line in the figure is the reference curve, which is the probe deformation curve formed after the probe contacts the smooth mica sheet surface, and the solid line is the probe deformation curve formed after the probe contacts and loads in the middle of the fiber. The deformation of the middle part of the fiber can be obtained by calculating the deviation between the two in the \( Z \) direction, and the fiber stress can be obtained by multiplying the elastic coefficient of the probe. The elastic modulus of the fiber is obtained.

![Figure 4. Relation between probe cantilever offset D and piezoelectric sensor displacement Z in fiber bending experiment.](image)
3. Results and discussion

3.1. Fiber morphology characterization
The morphology of PCL fiber was characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). Figure 5 is the SEM image of PCL fiber after spraying gold. It can be seen from the figure that the diameter of the fibers prepared with two concentrations of PCL solution is relatively uniform, and there is a bond between the fibers. Figure 5 (a) shows the fiber film obtained under the condition of 10 wt% solution concentration. The fiber density is denser and the fiber diameter is smaller than that of Figure 5 (b) when the concentration is 14 wt%.

![Figure 5. SEM image of PCL fiber, solution concentration is (a) 10 wt% (b) 14 wt% [15].](image1)

Further, AFM was used to characterize the structural characteristics of the fiber surface, and the image as shown in Figure 6 was obtained. It can be seen that the fiber surface has the characteristics of unsmooth transverse crisscross stripes, which is mainly due to the solidification of PCL solution in the air during the electrospinning process. At the same time, the orientation of the molecular chain changes under the axial tension of the electric field force, resulting in the change of the internal crystal structure of PCL and the formation of crisscross crystal structure. The crystallization characteristics on the fiber surface have an impact on its mechanical properties, especially the mechanical properties under microscopic conditions, which may cause the dispersion of experimental data. During the experiment, in order to reduce the dispersion of data, three points of each fiber were taken as data points, and then the data were weighted average.

![Figure 6. Images of PCL fibers obtained by AFM.](image2)
3.2. Tensile test results
A total of 40 groups of PCL fibers with different diameters were selected for tensile test, and the results of elastic mechanical properties of axial tensile fibers were obtained, as shown in Figure 7. It can be seen from the figure that the elastic modulus of the fiber is basically distributed in a range, about 0.3 to 0.7 GPa, and there is no obvious change trend between the elastic modulus of the fiber with different diameters and the fiber diameter. The elastic modulus of the fiber with diameter more than 1 μm is about 0.5 GPa, while that of the fiber with diameter less than 1μm is discrete. With the decrease of fiber diameter, the dispersion degree of tensile elastic modulus becomes higher and higher. The reason of the above experimental results may be related to the existence of complex surface morphology characteristics on the fiber surface. For the fiber with diameter more than 1 micron, the surface structure is mainly layered structure, which has weak tensile properties due to non orientation; for the fiber with diameter less than 1 micron, the surface structure is mainly molecular oriented fiber This kind of structure has good tensile properties and high elastic modulus. According to the difference of fiber structure, the smaller the fiber diameter is, the greater the influence of the internal structure characteristics on the tensile modulus is.

![Figure 7. Variation of elastic modulus with fiber diameter in tensile test of PCL fiber.](image)

3.3. Bending test results
A total of 23 groups of fibers with different diameters were selected for bending test. The results of fiber mechanical properties obtained by bending experiment are shown in Figure 8. It can be seen from the figure that there is a correlation between the fiber elastic modulus and the fiber diameter. When the fiber diameter becomes smaller, the bending elastic modulus of PCL increases continuously. For the fibers with diameter over 190 nm, the elastic modulus in bending test is basically the same, while for the fibers with diameter less than 190 nm, the bending elastic modulus increases significantly. The reason for the above experimental results may be related to the different crystal morphology in the fiber. For the fibers with smaller diameter, the axial tension is more intense during the forming process, so the crystallinity will increase, which shows a higher elastic modulus in the bending experiment; while for the fibers with larger diameter, the crystallinity is lower, which shows a lower elastic modulus in the experimental process. There is still controversy about the explanation of the scale effect of fiber materials in bending experiments. Some scholars believe that the surface effect of materials leads to the scale effect of material mechanical properties in the micro environment. With the decrease of material scale, the specific surface area of materials increases, and the effect of surface tension on the mechanical properties of materials can not be ignored [16]. Some scholars believe that in the process of material deformation, strain gradient will affect the mechanical properties of the material, and for the bending experiment, the effect of strain gradient is more significant, so it will lead to the scale effect found in the experiment [17].
4. Conclusion

PCL fibers with different diameters were prepared by electrospinning. The surface morphology of PCL fibers was analyzed by scanning electron microscope (SEM) and atomic force microscope (AFM). The mechanical properties of PCL fibers were measured by axial tensile test and three-point bending test. The results show that the fiber surface has the characteristics of non-uniform transverse cross stripes, and the mechanical properties of the fiber show discrete distribution in the tensile process. However, in the bending experiment, the mechanical properties of the fiber show a correlation with the size of the fiber diameter, and the quantitative relationship between the two needs to be further studied. The above research is expected to provide research basis for further understanding the mechanical properties of electrospun fibers.

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