

静电纺丝法和气流-静电纺丝法制备聚砜纳米纤维*

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摘 要 应用电纺法制备了聚砜纳米纤维.设计了一种新型的气流/静电纺丝装置,其特点是在喷丝头上添加了喷气组件.电纺过程中所用聚砜的特性粘数为 0.97 dL/g,溶剂为二甲基乙酰胺,载气为氮气.研究了聚砜纳米纤维的平均直径与过程参数之间的关系.研究表明影响聚砜纳米纤维的平均直径的主要因素为电压、纺丝液的流速、喷丝头与收集器之间的距离、操作温度以及纺丝液的性质(如粘度、表面张力和电导率).纳米纤维的平均直径和直径分布用扫描电镜表征.应用这种气流/静电纺丝法制备的纳米纤维的直径范围是 50 ~ 500 nm.所得纳米纤维的直径依赖于电压、喷丝头与收集器之间的距离以及喷丝液的浓度.结果表明,采用气流/静电纺丝不仅能制备较细而且均匀的纳米纤维,而且产量更高.

关键词 静电纺丝,聚砜,纳米纤维,气喷,电纺装置

纳米纤维由于其独特性能已引起了科学界和产业界的普遍关注,国内外已有大量的研究报告^[1-5].纳米纤维的制备方法很多,其中电纺是产生聚合物纳米纤维的一种直接方法.当聚合物溶液或聚合物熔体表面上的电力克服其表面张力时,带电射流产生喷射.射流拉伸成一直线至一定距离,然后弯曲,进而循环形或螺旋形路径行走.静电力使射流伸长数千倍甚至数百万倍,于是射流变得非常细.同时,借溶剂挥发或熔体冷却,射流固化为丝条,在适当的条件下丝条直径为 50 ~ 500 nm.所得的纳米长纤维通常以无纺布的形式收集于与地线连接的金属板、缠绕器或其它收集器上.

聚合物溶液的电纺可以追述到 1934 年, Formhals^[6]发明了用静电力制造聚合物纤维的工艺.该纤维是由醋酸纤维素溶液形成.所需的电压差取决于纺丝溶液的性质如分子量和粘度. Gladding^[7]和 Simons^[8]改进了电纺设备,并生产出更稳定的纤维.他们应用象连续式输送带一样的可运动装置来收集纤维.稍后, Bornat^[9,10]申请了另外一个电纺装置的专利,在这个装置的旋转轴上有一个可移动的收集器.最近, Chu^[11]等进一步改进电纺设备,应用双电场产生导电聚合物射流,纺制纳米纤维. Deitzel^[12]等为了解决射流的不稳定性,在喷丝头与收集器间设置多个带电环来改变电力线的微观形态,控制纤维的沉积路径.

Reneker 和 Doshi^[13]由水溶性聚氧乙烯制得直径为 0.05 ~ 5 μm 的电纺纳米纤维.描述了电纺工艺、工艺条件、纤维形态和电纺纤维的一些可能用途. Kosuke^[14]用静电纺丝法制备了丝蛋白无纺纳米纤维,研究了制备的最佳条件,同时研究了所得纳米纤维的直径分布.其余数十种材料的静电纺丝可见有关专著^[1,2].

本文发展了一种新型静电纺丝机,即气流-静电纺丝机(简称气-电纺机).在原有电纺机的基础上,增加气路系统,应用静电力和气流与聚合物射流间的摩擦力的合力对射流进行拉伸,得到均匀的纳米纤维.同时,以聚砜为例,研究了高分子材料的静电纺丝和气流-静电纺丝的差别,以及聚砜静电纺丝中基本过程参数对所制备纳米纤维的直径及其分布的影响.

1 实验部分

1.1 气-电纺机的结构

气-电纺机如图 1 所示,它是由供样系统、喷丝头、高压系统、供气系统和收集系统组成,与标准的电纺机喷丝头仅有纺丝流体的毛细孔结构不同.气-电纺机具有的喷丝头结构还包括气体射流通道的,如图 2 所示.气流进入喷丝头,通过缓冲区使气流稳定,从射流孔以层流的方式喷射到环境空气中.高分子溶液则由注射器慢速挤入毛细管中,流经一定长度的毛细管,由于溶液的表面张

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力,可在毛细管口形成喷射流。

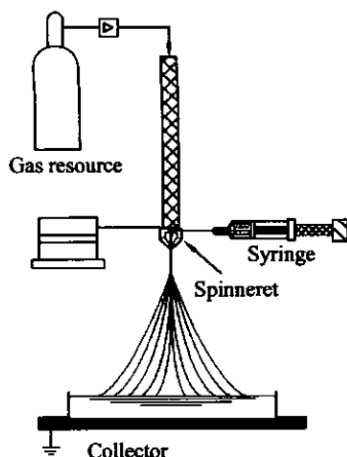


Fig. 1 Schematic diagram of gas-jet/electrostatic spinning set-up

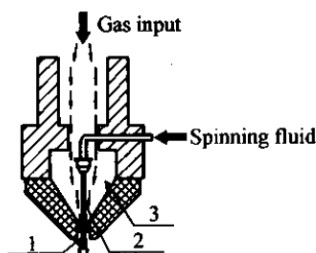


Fig. 2 Schematic diagram of spinneret used in gas jet/electrostatic spinning setup

1) Orifice; 2) Capillary; 3) Gas Buffer

要实现气-电纺,可将一定浓度的聚合物溶液置于进样器中,通过喷丝头导出聚合物溶液,喷丝头与高压系统的正极相连,在喷丝头下端有一金属收集网或凝固浴,为负极,并且接地。在适当的条件下,主要是适当控制纺丝液的性质(粘度、表面张力和电导率)及操作条件(电压、流体速率、温度、毛细管与收集器间的距离和气体参数)。从毛细管中流出的纺丝液射流,在气流力和静电力的作用下加速运动,并分裂而形成微细流簇,溶剂挥发,凝固或固化成细丝,以无纺布的形式沉积在收集器上。在收集器的凝固浴中,由于相转化,使纤维中的溶剂转移到凝固浴中,不会产生纳米纤维的再聚集。

1.2 材料与方法

聚砜(PSU)是由安化公司提供,特性粘数 $[\eta] = 0.97 \text{ dL/g}$;溶剂为二甲基乙酰胺(DMAc),分析纯,上海化学试剂厂;氮气为工业级。气-电纺机,本研究小组自行设计制造。扫描电镜,JSM-5900LV(JEOL公司制造)。

用于纺丝的溶液是将在 105°C 下干燥 30 h 的

PSU 配制成 10% ~ 20% 二甲基乙酰胺溶液。高压电源提供 27 ~ 50 kV 的电压,电源的正极接喷丝头,负极接收集器,收集器接地。15 kPa 高压氮气用 PP 管接进气管。用气体流量计测定气体流量约为 10 L/min。将聚合物溶液 10 mL 装入 20 mL 注射器中,采用螺杆驱动器驱动注射器,将聚合物溶液输入喷丝头,进样速度为 $9 \mu\text{L/s}$ 。喷丝头中,毛细管的内径为 0.4 mm。在其他条件固定时,改变喷丝孔与收集器之间的距离,以确定其对纳米纤维直径的影响。用扫描电镜观测气-电纺纳米纤维形态和直径。图像处理采用 SigmaScan Pro 2.0 图像分析软件。

2 结果与讨论

2.1 电纺和气-电纺结果的比较

从表面现象的研究可知,电纺过程中,在毛细管顶端的液滴,将成为凸形的半球状,当在液滴表面上施加某一电位,液滴曲面的曲率将逐渐改变,当电位达到某一临界值时,半球状液滴会转变为锥形,其锥形的角度为 49.3° ,这一带电的锥体称为 Taylor 锥^[15],在强电场作用下,流体进而可以从 Taylor 锥中被顶出,形成射流,这一带电射流在电场中进一步加速,直径减小,如图 3(a)。

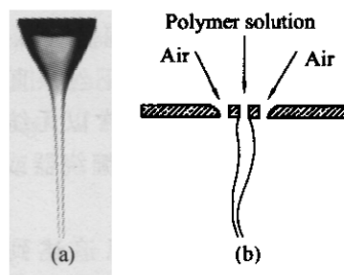


Fig. 3 Principle of drawing in traditional electrospinning and gas-jet/electrostatic spinning

a) Drawing by electrostatic force; b) Drawing by gas jet

纺丝过程力学分析的理论基础是由 Ziabicki^[16]系统提出的。在此基础上,Shambaugh^[17]进行了气流拉伸中丝条形变的力学分析,如图 3(b)。与此对应,静电纺丝中纺丝射流的形变则主要是由带电射流的各种不稳定性所致^[18-20]。完整分析气-电纺中射流的力学,显然应将气流纺和静电纺丝的理论正确结合起来,我们正在进行此项工作,这里仅报道实验的主要结果。

气-电纺和电纺实验参数已在图 4 的说明中注明。由此图可以看出,气-电纺纳米纤维的直径为 200 nm,与电纺纳米纤维的平均直径(350 nm)

相比较,明显变细.这进一步证实了气流在纺丝过程中起到的拉伸作用.从图4中纳米纤维直径分布图的比较可知,电纺纤维的直径分布在200~700 nm范围,而气-电纺纳米纤维的直径分布在

100~600 nm范围.而且气-电纺纳米纤维的直径分布比纯电纺纳米纤维的直径分布窄,主要集中在100~300 nm.

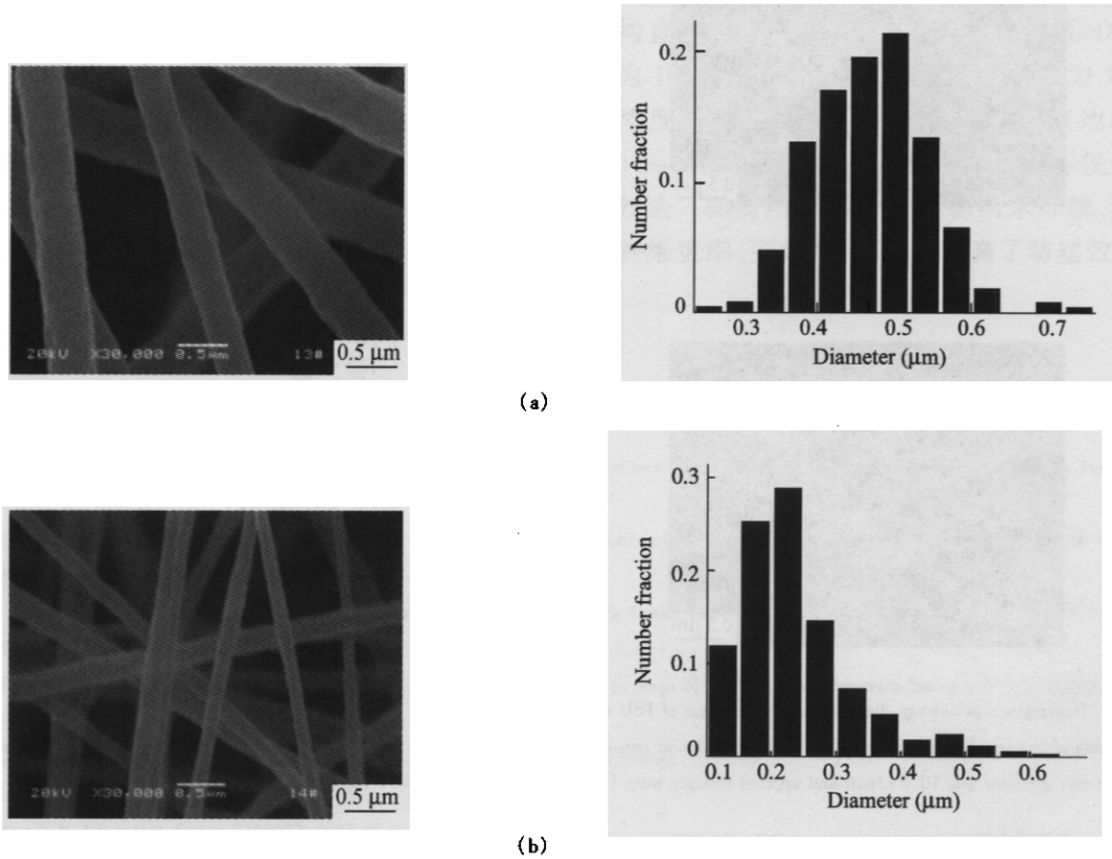


Fig. 4 SEM photographs and image manipulation graphs of PSU nanofibers spun by (a) electrospinning and (b) gas-jet/electrostatic spinning. Parameters of gas jet/electrostatic spinning were that solution concentrations of PSU/DMAc were 20%, distances between the spinneret and collector were 19 cm, gas flow was 10.0 L/min and applied voltages were 32.5 kV, respectively.

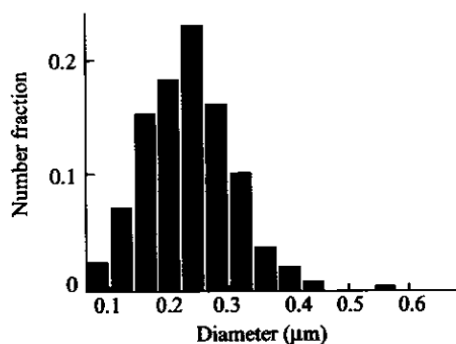
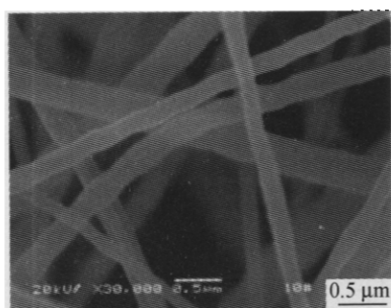
2.2 纳米纤维直径与过程参数的关系

2.2.1 施加电压对纳米纤维直径及直径分布的影响 当其他参数维持不变时,不同电压下得到纳米纤维的扫描电镜照片如图5和图4(b)所示.图5(a)、图4(b)和图5(b)分别表示施加电压为27.5、32.5和45.0 kV.在本实验条件下,随着电压从27.5增加至45.0 kV,纳米纤维的平均直径从250 nm降至150 nm.这是由于随着电压增加,高分子纺丝溶液的射流有更大的表面电荷密度,因而有更大的静电斥力,同时,更高的电场强度使射流获得更大的加速度.这两个因素均能引起射流及形成的纤维有更大的拉伸应力,这导致有更高的拉伸应变速率,有利于得到更细的纤维.但是,直径随电场的改变不很大.

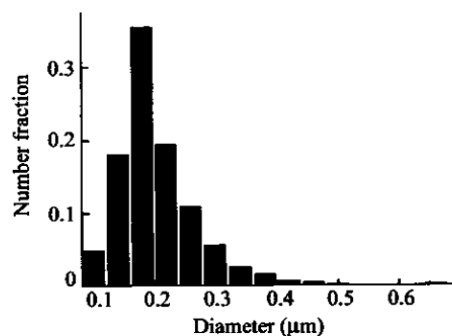
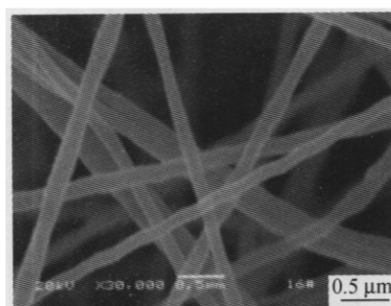
2.2.2 喷丝孔与收集器之间距离对纳米纤维直径及直径分布的影响 当其他参数维持不变

时,不同喷丝头与收集器之间的距离纺得 PSU 纳米纤维的扫描电镜照片如图6所示和图4(b).图6和图4(b)分别表示的喷丝头与收集器之间的距离为15 cm和19 cm,随着喷丝头与收集器之间的距离增大,所得纳米纤维直径减小.当喷丝头与收集器之间的距离由15 cm增加至19 cm时,PSU 纳米纤维的平均直径由300 nm减小至150 nm(见图6和图4b).同时,由于喷丝头与收集器之间的距离的减小,纤维在喷丝头与收集器间的飞行距离缩短,纤维的分裂次数和拉伸倍数减小,纤维直径增大.

2.2.3 纺丝原液浓度对纳米纤维直径及直径分布的影响 PSU 的 DMAc 纺丝原液浓度对纳米纤维直径的影响如图7和图4(b)所示. PSU/DMAc 浓度为10%时,所得纤维的平均直径约为130 nm(图7),当浓度增加至20%时,纤维直径相应地增



(a)



(b)

Fig. 5 Dependence of average diameter and distribution of PSU nanofiber on voltages

Parameters of gas jet/electrostatic spinning were that solution concentrations of PSU/DMAc were 20%, distances between the spinneret and collector were 19 cm, gas flow was 10.0 L/min and applied voltages were (a) 27.5 kV; (b) 45.0 kV, respectively.

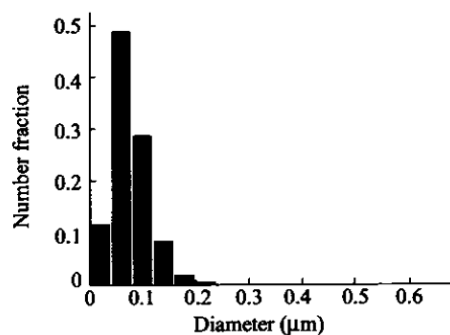
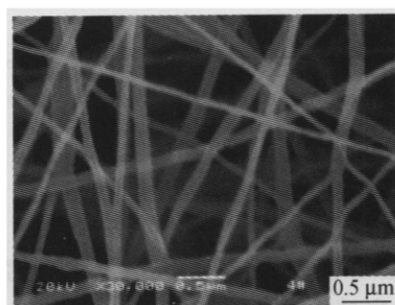
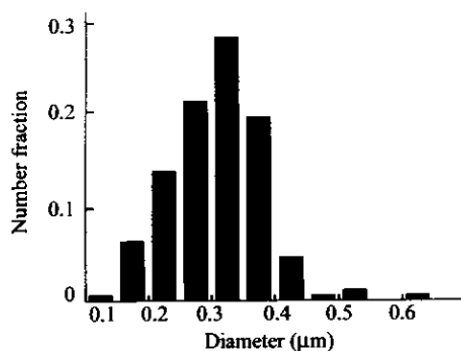
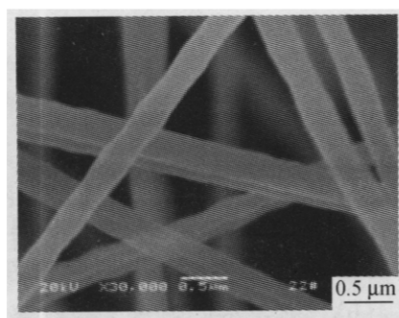


Fig. 7 Dependence of average diameter and distribution of PSU nanofiber on concentration

Parameters of gas jet/electrostatic spinning were that distances between the spinneret and collector were 19 cm, gas flow was 10.0 L/min and applied voltages were 32.5 kV, and solution concentrations of PSU/DMAc was 10%.

Fig. 6 Dependence of average diameter and distribution of PSU nanofiber on the gap between spinneret and collector

Parameters of gas jet/electrostatic spinning were that solution concentrations of PSU/DMAc were 20%, applied voltages were 32.5 kV, gas flow was 10.0 L/min and distances between the spinneret and collector was 15 cm.

大至 250 nm(图 4b)。由于高分子溶液的浓度包含了许多纺丝溶液的材料参数,如表面张力和黏度等。高分子溶液的浓度增加,则使高分子溶液的表面张力和黏度均相应地增加,这使得纺丝过程中,气流拉伸力和静电力需要克服的阻力增大。在相同条件下,射流的分裂次数和拉伸倍数均会下降,从而得到较粗的纤维。

根据纺丝原理,在聚合物纳米纤维制备的静电纺丝法的基础上,发展了新型聚合物纳米纤维的制备方法,即气流-静电纺丝法。制备了直径范围在 50 ~ 500 nm 之间的 PUS 纳米纤维。气流-静电

纺丝的过程参数对纳米纤维直径有明显的影响。电压从 27.5 增加至 45.0 kV 时,纳米纤维的平均直径从 250 nm 降至 150 nm;喷丝头与收集器之间的距离由 19 cm 减小至 15 cm 时,PSU 纳米纤维的平均直径由 150 nm 增加至 300 nm;PSU/DMAc 浓度为 10% 时,所得纤维的平均直径约为 130 nm,当浓度增加至 20% 时,纤维直径相应地增大至 250 nm。研究表明,气流-静电纺丝法不仅与静电纺丝法一样能用于制备聚合物纳米纤维,而且所得纤维更细、更均匀,同时还提高了纺丝效率。

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POLYSULFONE NANOFIBERS PREPARED BY ELECTROSPINNING AND GAS-JET/ELECTROSPINNING

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Abstract Polysulfone nanofibers were prepared by electrospinning. The electrospinning equipment was designed in a new way, in which the spinneret was combined with a gas jet device. The intrinsic viscosity of the used polysulfone was 0.97 dL/g in dimethyl acetamide, which was also the solvent in electrospinning. The gas used in this gas jet/electrostatic spinning was nitrogen. The relationship between the process parameters and the average diameter of polysulfone nanofibers was investigated. The main process parameters studied in this work were the voltage, the flow rate of the spinning fluid, the distance between the spinneret and the nanofiber collector and the temperature in the spinning chamber. The other important factors determining the nanometer diameter were the spinning fluid properties including its viscosity, surface tension and electrical conductivity. The average diameter and the diameter distribution of electrospinning nanofibers were measured experimentally by using scanning electron microscopy. The diameter of polysulfone nanofibers prepared by the gas jet/electrostatic spinning was in the range from 50 nm to 500 nm. It was found that the diameter of nanofibers was mainly depended on the high voltage, the gap between the spinneret and the collector and the concentration of polymer solutions. As compared to the conventional eletrospinning the gas jet/electrostatic spinning method could generate thinner and more uniform nanofibers with higher efficiency.

Key words Electrostatic spinning, Polysulfone, Nanofibers, Gas jet, Electrospinning equipment