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厦门大学

博 士 学 位 论 文

微尺度韦森堡效应及输运特性的实验研究

Experimental Study on the Microscale Weissenberg Effect for Pumping Appliations

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摘　要

基于电液耦合原理的静电纺丝直写可按需喷印多种材料，实现高精度图案化沉积，被认为是一种极具潜力的微纳增材制造技术。现有的静电纺丝供液存在时滞长、压阻幅度大等问题，无法满足电纺直写的连续、稳定、响应快速的液体输运需求，制约了其在微纳制造领域的应用与发展。因此，本文以电纺直写供液为目标，展开了对微尺度包轴效应、微纳流体包轴输运以及强电场作用下的包轴效应的研究，探索了基于液体包轴输运的电纺直写技术在微纳制造、柔性电子领域中的应用。为此，围绕这几个关键问题开展了如下研究工作：

搭建包轴效应供液装置，实现了针芯高精度对中装配，获取针芯振幅小于10μm 稳定旋转运动，达到直写的供液要求。从实验和理论研究宏—微尺度包轴效应，分析不同溶液、转轴转速等对包轴效应的影响。研究结果表明，微尺度下稳态包轴效应源于剪切作用产生的包轴爬升力，是表面张力、包轴爬升力、离心力耦合作用结果，其中针芯最大转速~ $1/\sqrt{R}$（R 为针芯半径），包轴爬升力 $N_{zz}\sim\omega^2(R/r)^{4/n}$、离心力 $F\sim\rho\omega^2R^{4/n}r^{4/n-1}$（$r$ 为液面与转轴中心的距离，n 是流体的非牛顿指数，ρ为流体密度，针芯转速ω）。

研究分析了宏—微尺度包轴效应中的表面张力作用。实验结果显示，表面张力对宏观包轴效应影响远小于微尺度包轴效应。通过调节活性剂浓度、管道内径、针芯直径和表面特性等参数，改变表面张力大小、接触角和液面倾角，探究其在包轴效应和包轴输运中的作用。研究发现，表面张力是微尺度包轴形貌和供液速度的重要影响因素，也是微尺度管芯结构实现稳定长距离液体包轴输运的关键。

为更清晰地了解管道内部的包轴效应中剪切流变作用，提出微尺度双杆结构(管芯结构的简化)包轴效应，实现微流体无管输运，大幅提高液体输运效率。考察溶液浓度、针芯转速、双杆间距及针芯直径等参数对包轴效应的影响，研究双杆包轴效应中表面张力和剪切力的作用。对管芯结构中剪切流变行为的理论和实验进行研究，得到该结构中包轴爬升力 $N_{zz}\sim\omega^2/[n(1-2A^{2/n})^2]$（其中 A 为针芯直径与管道内径的比值），供液速度 $Q\sim\omega(1-A)^{2+1/n}/(1-2A^{2/n})$，与针芯转速成正比。从理论和实验上证实了管芯结构能实现精确、稳定、快响应的液体包轴输运。此外，对电场强度、针芯旋转速度和管道内径等工艺参数对射流的影响进行了分析，

实验和仿真研究了剪切流变作用与稳态射流之间的相互关系。

首次研究基于液体包轴输运的电纺直写技术在石墨烯喷印领域的应用。微尺度液体包轴输运将石墨烯墨水制造和沉积融为一体，避免石墨烯团聚现象，提高了石墨烯的产率和质量。调整各项工艺参数，图案化沉积 100～1000μm 线宽的高电导率石墨烯复合材料薄膜，制备压力、湿度敏感单元并验证其性能。为柔性基材上石墨烯结构制备提供了一种新技术。

关键词：微尺度；包轴效应；电纺直写；石墨烯喷印

Abstract

Electrohydrodynamic direct writing can be used for high precision patterned deposition of a variety of materials, therefore it is considered as a technology with great potential for micro/nano additive manufacturing. As is well-known, there are some problems in solution supplying of concentional electrospinning technology, such as the big time lag and great fluid flow resistance. So it can't be realized the continuous, stable and fast response of liquid transportation which is required by the direct writing technique, limiting the electrohydrodynamic direct writing technology application and development in the micro/nano manufacturing field. Therefore, to address the demand of solution supplying for direct writing, the microscale Weissenberg Effect, micro- and nanoscale fluid pumping application based on microscale Weissenberg Effect, the microscale Weissenberg Effect in strong electric field were studied in this article. Finally, the applications of pumping based on microscale Weissenberg Effect were studied for micro/nano manufacturing and flexible electronics. Therefore, research works were carried out corresponding to the above aspects:

The pump device based on microscale Weissenberg Effect was builded, which overcomes the difficulty of position and stability of rotation needle. In our device the amplitude of needle is diminished to less than 10μm, which ensures the stable pumping by rotating needle. The research works of the microscale Weissenberg Effect based on theoretical analysis and experiments, the influences of different solution, the rotating speed on the microscale Weissenberg Effect were analyzed. Then we found that the microscale Weissenberg effect which originates from shear force is the result of surface tension, climbing and centrifugal force coupling. The maximum rotating speed in steady microscale Weissenberg effect $\sim 1/\sqrt{R}$ (here R is the radius of rotation needle), climbing force $N_{zz} \sim \omega^2 (R/r)^{4/n}$, centrifugal force $F \sim \rho\omega^2 R^{4/n} r^{4/n-1}$ (here r is the distance between axis of rotation needle and fluid, n is non-Newtonian index, ρ is the density of fluid，rotation speed is ω). The velocity distribution based on Weissenberg effect is obtained by concentric tube model.

The surface tension in Macro and micro scale Weissenberg effect was studied. The experimental results show that the effect of surface tension on macrosacle is far less than the effect of it on microscale. The effects of surface tension, contact angle and surface angle on micro- and nanoscale fluid pumping application based on microscale Weissenberg Effect were studied by adjusting the parameters such as the concentration of the active agent, the diameter of the pipe, the diameter of the needle and the surface properties. It is found that the surface tension is an important influence factor of the microscale Weissenberg effect and pumping based on Weissenberg effect. It is also the key factor to achieve the stable pump in the microscale tube-core structure.

In order to more clearly understand the shear rheological properties based on the microscale Weissenberg effect in pipe, A pump that content double pole structure (the simplified tube-core structure) based on microscale Weissenberg effect has been proposed and studied. This pump without pipe greatly improves the efficiency of liquid transport. By investigating the effect of the parameters such as the concentration of solution, the rotating speed, the distance between rods and the diameter of the needle on the microscale Weissenberg effect, the mechanism of the surface tension and shearing force impact on double rod Weissenberg effect was studied. According to the theoretical and experimental study on the shear behavior of the tube-core structure, the climbing force in microscale Weissenberg effect $N_{zz}\sim\omega^2/[n(1-2A^{2/n})^2]$（Here A is the ratio of pipe diameter and the diameter of needle）, flow rate $Q\sim\omega(1-A)^{2+1/n}/(1-2A^{2/n})$, flow rate is $Q\sim\omega(1-A)^{2+1/n}/(1-2A^{2/n})$,proportional to the rotating speed. Both in theory and experiment confirmed the tube-core structure can realize accurate, stable and quick response of liquid transport based on Weissenberg effect. In addition, we observed the impact of parameters such as electric field intensity, needle core rotate speed and pipe diameter on the jet flow, and then created the relationship between rheological shear effect and jetting steady by experiment and simulation analysis.

The first application of pumping based on Weissenberg effect is realized in the

field of graphene jet printing. The production and sedimentation of graphene ink were integrated by microscale liquid axis packaged feeding which avoids the agglomeration of graphene. This method improves the yield of graphene and quality and simplifies graphene's printing process. Using cheap materials such as graphite, PEO, SDS, we fabricated several functional structures such as high conductivity graphene composite membrane and pressure or humidity sensitivity unit with 100 ~ 1000 microns line width by adjusting the process parameters. This method provides a new technology to fabricate the structure of graphene on flexible substract.

Keywords: Microscale; Weissenberg effect; Electrohydrodynamic Direct-Writing; graphene jet-Eject

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第一章 绪论

喷印技术能进行快速、高质量的打印，对喷印材料、打印介质等要求较低，被认为是目前最主要的印刷技术。得益于多学科的快速融合，喷印技术在非传统领域也取得了巨大的发展，逐渐应用于柔性电子、微纳制造、生物医疗、3D 打印等领域。而传统的热发泡[1-3]、微压电等喷印方式[4,5]，已经不适应新领域对喷印材料、打印介质、打印精度等方面的各种要求，需要进行改良。基于电液动力学的电纺直写技术工艺简单，成本低廉，克服了传统喷印方式的缺陷，可应用于高粘度材料，并且能形成直径远小于喷嘴尺寸的射流，制造出微米甚至是纳米级别[6,7]的结构，在生物医疗[8-12]，3D 打印[13,14]，光电器件[15-23]等领域存在巨大的潜力。

然而，随着微纳米制造技术的发展，电纺直写技术需要面对更高粘度，更小尺度的溶液喷印需求。因此需要对现有的供液技术进行改进，提高高粘度溶液的供液精度和响应速度，增强对射流的调控能力，促进电纺直写技术在各个领域应用发展。

1.1 电液耦合喷印技术

电液耦合喷印技术利用电场力对溶液进行拉伸，使之发生形变，并克服表面张力形成射流，最终沉积在收集板上形成微纳米纤维（静电纺丝）或者液滴（静电雾化）。它利用外界电场力拉伸溶液，避免了喷头处液体粘滞力的阻碍以及挤出胀大效应[24,25]，从而实现高粘度溶液的微纳米喷印。

1.1.1 电液耦合喷印原理

如图 1-1，电液耦合喷印系统主要由高压电源、喷头、收集板等组成[26]。聚合物溶液由注射泵推动，在喷嘴末端形成悬滴，最终在高压电场的作用下形成纤维或液滴。

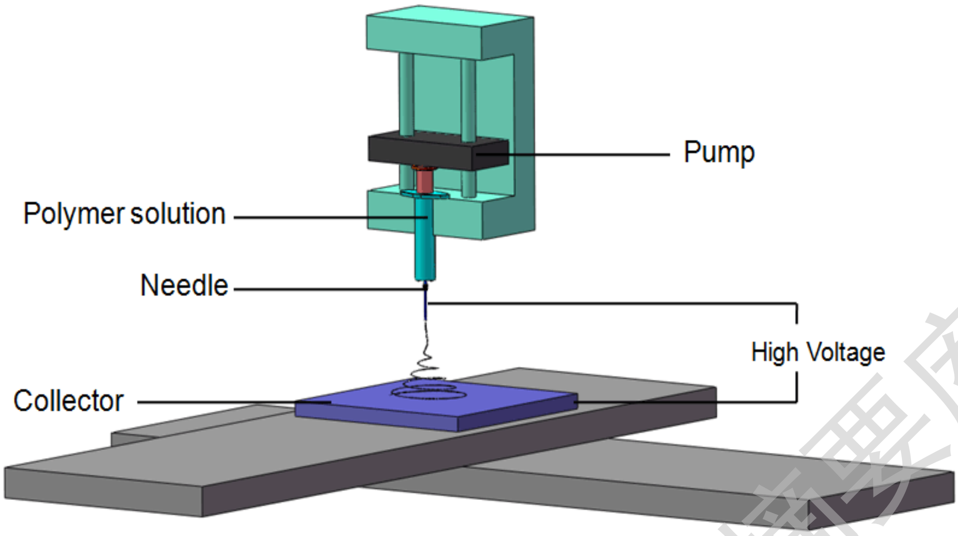

图 1-1 电液耦合喷印的实验装置原理图

相比传统的喷印技术，电液耦合喷印的过程实质是电荷诱导的自组装过程[27]。其来源于静电学中的恩绍定理。该定理认为流体中不可能存在完全由电荷的静电相互作用构成的一个稳定静止的力学平衡结构。因此喷射流体中的电荷控制着带电聚合物沿着复杂的路径运动，使得流体中的静电能变得最小，即自组装过程[28,29]。该过程中，当溶液的粘性较小时，会形成微小带电液滴，即静电喷雾；当溶液的粘性较大时，溶液会被拉伸，最终形成纤维状沉积物，即静电纺丝。

（1）静电纺丝

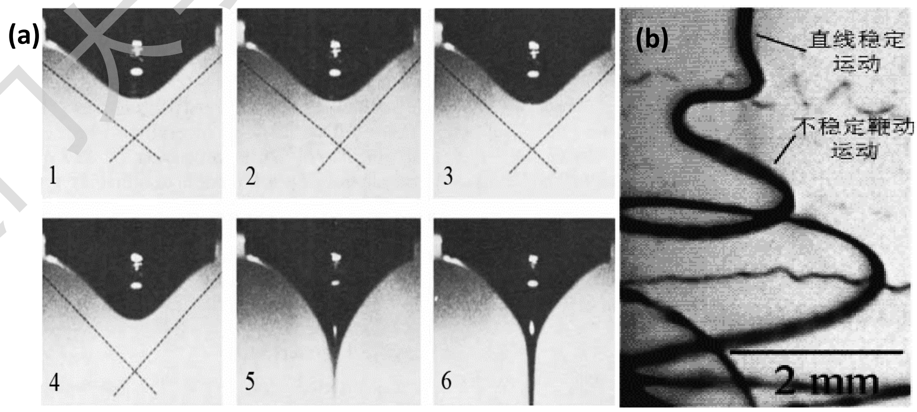

图 1-2 静电纺丝的自组装过程 (a)喷头处液滴的形变[30]; (b)射流的运动过程[31]

在静电纺丝领域中，需要关注的不仅是电纺纳米纤维直径的变化，也包括由珠链结构导致的纤维直径的波动 [32,33]。电纺的自组装过程形成了各种形状的纤