J. Non-Newtonian Fluid Mech. 153 (2008) 95–108

Journal of Non-Newtonian Fluid Mechanics

www.elsevier.com/locate/jnnfm

Modeling of non-isothermal polymer jets in melt electrospinning

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Received 6 October 2006; received in revised form 27 November 2007; accepted 30 November 2007

Abstract

We have developed a model for non-isothermal, free surface flows of electrically charged viscoelastic fluids in the stable jet region of the melt electrospinning process. The model is based on thin filament approximation applied to fully coupled momentum, continuity, and energy equations, Gauss' law, and the non-isothermal Giesekus constitutive model. The asymptotic jet thinning relationship widely used in previous electrospinning models was found not applicable for the case of polymer melts. The underlying assumption of the balance of inertial and electrical forces in the asymptotic region does not hold for typical melts which exhibit high tensile forces throughout the spinning region, particularly under non-isothermal conditions. We have developed a new initial thinning condition for fluids with low electrical conductivity and high viscosity based on a force balance near the nozzle. The resulting system of equations is solved numerically and the simulated initial jet profiles are compared to digitized experimental images of the stable melt jet near the spinneret. In addition, the predicted effects of melt temperature, flowrate, and electric field strength on the final jet diameter are compared to the final average fiber thickness from non-isothermal experiments where the whipping motion has been suppressed by rapid cooling. The simulation results are in good quantitative agreement with the flow visualization experiments on electrospinning of polylactic acid (PLA) melt under various spinning conditions.

Keywords: Non-isothermal; Electrospinning; Polymer melt; Giesekus model

1. Introduction

As the nanotechnology revolution spreads to encompass practically every aspect of modern manufacturing, it sets extremely demanding and technologically difficult goals. These goals often require the revival of old concepts such as electrospinning that have not been exhaustively studied or industrially assimilated. The current study is driven by the demand for submicron-sized fibers with high surface area to mass ratios to be used in high performance filtration, biological and biomedical fields, and in the chemical industry [1–3]. It has been shown that submicron fibers can be readily produced using electrospinning, which utilizes applied electric field to accelerate and drastically elongate a charged fluid jet. While most of the previous work on electrospinning has involved polymer solutions, much progress has also been made in polymer melt electrospinning [4–7]. The latter is more attractive for industrial applications because it is environmentally benign, it eliminates the solvent recovery and treatments costs, and there is a wider selection of polymers available, including such important systems as polyethylene (PE) and polypropylene (PP) which do not have appropriate solvents at room temperature. Besides above advantages, this solvent-free approach also opens the door to theoretical routes to model electrospinning without the complications associated with solvent evaporation.

In conventional electrospinning, a charged polymer jet undergoes rapid initial thinning in a "stable jet" region, as it is introduced into the spinning region (see Fig. 4). Further down the stream, bending and whipping instabilities cause a "whipping motion" which further thins the jet prior to its arrival and solidification on a collector plate [8–11]. The complexity of the electrospinning process has been the stumbling block in its further development, optimization, and incorporation in the industrial scale applications. The experimental work in this field sets some guidelines and general trends in the resulting fiber sizes and size distributions, but is insufficient to optimize the process. Although a number of theoretical approaches have also been proposed, none rigorously account for the polymeric nature of the materials of interest and consider the full complexity of the experimental setup. The stable jet region

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0377-0257/$ – see front matter
doi:10.1016/j.jnnfm.2007.11.011

has been examined in the following works. Spivak and Dzenis developed a 1-D model with a power law fluid [12]. Hohman et al. utilized the concept of a "leaky dielectric" model to refine the model and account for the interaction of the surface charges in the jet with the external applied electric field, but considered only Newtonian fluids [11]. Feng further expanded the model by incorporating the Giesekus constitutive model to account for the viscoelastic behavior of polymer solutions [13,14]. Feng also proposed a modified version of the electric field equation that introduced a new parameter (electrical current), but resolved an issue with an uncertain boundary condition on surface charge density at the inlet, which at times caused an unphysical long-wave instability of the jet. Carroll and Joo revisited Feng's model and verified its predictions by an in-depth comparison to a variety of experimental results from polymer solution electrospinning [15]. The whipping motion region has been addressed by Reneker et al. [8,9], and Hohman et al. [10,11]. Instability models were developed to describe the whipping phenomena. No analogous non-isothermal models, required for melt electrospinning simulation, have been proposed to date. It is also desired to compare the characteristics of melt electrospinning and those of conventional melt spinning [16–20].

In the current study, we extend the previous treatment by Carroll and Joo to the case of non-isothermal polymer melt jet and compare the simulation results to experiments on polylactic acid (PLA). PLA is a non-toxic biodegradable polymer, and its nanofibers will find use in a number of important applications such as wound dressings and environmentally safe packaging. The absence of mass transfer in melt electrospinning allows for more rigorous modeling, but other complications arise. Previous work [4–7] has shown that fibers electrospun from melt tend to be much thicker and less uniform than those from solution because of the lack of additional thinning due to solvent evaporation and potentially reduced whipping motion due to lower electrical conductivity of the melt. These factors further amplify the importance of thinning optimization in the stable jet region. In fact, experiments suggest that contrary to previous preconceptions a significant degree of thinning can occur in the stable jet region. One of the main factors affecting the jet thinning is extensional viscosity, which in the case of a melt is controlled by the fluid temperature and molecular architecture. In experiments, the temperature field can be manipulated, but is usually non-uniform throughout the spinning region. This added complexity further complicates the model and calls for the non-isothermal treatment of the problem. The present simulation model is based on the thin filament (1-D) treatment previously used by Spivak and Dzenis, Feng, and Carroll and Joo [12–15]. Momentum, continuity, and charge conservation equations are coupled with the energy equation and the electric field around an isolated needle. The Giesekus constitutive model modified to its non-isothermal form by time-temperature superposition [20] is used to account for the viscoelastic behavior of the melt at various temperatures. We also note that the underlying assumption of the balance of inertial and electrical forces in the asymptotic region does not hold for typical melts which exhibit high tensile forces throughout the spinning region, particularly under non-isothermal conditions. We propose a new initial thinning condition for fluids with low electrical conductivity and high viscosity based on a force balance near the nozzle.

Qualitative trends in model predictions are investigated while varying the parameters affecting viscoelasticity, shear thinning, viscosity, flow rate, and electric field. The model is studied under isothermal and non-isothermal conditions, and a comparison to experimental observations under various thermal profiles and acceleration potentials is presented.

2. Modeling procedure

2.1. Governing equations

The present continuum level model for the stable jet region (see the inset in Fig. 4) is developed by fully coupling the conservation of mass, momentum, charge, and energy equations with a viscoelastic constitutive model and the electric field equation at steady state. As in the other relevant studies discussed earlier, we utilize the thin filament approximation to obtain a simpler and more tractable solution. This is done by appropriately averaging the model variables across the radial direction.

The basic governing equations for isothermal simulations have been presented by Carroll and Joo [15]:

$$\text{Continuity:} \quad \pi R^2 v = Q, \tag{1}$$

$$\text{Momentum:} \quad \rho v v' = \rho g + \frac{F_T'}{\pi R^2} + \frac{\gamma R'}{R^2} + \frac{\sigma\sigma'}{\varepsilon_0} + (\varepsilon - \varepsilon_0) E E' + \frac{2\sigma E}{R}, \tag{2}$$

$$\text{Charge:} \quad \pi R^2 K E + 2\pi R v \sigma = I, \tag{3}$$

$$\text{Electric field:} \quad E(z) = E_\infty(z) - \left[\frac{1}{\varepsilon_0}(\sigma R)' - \left(\frac{\varepsilon}{\varepsilon_0} - 1\right)\frac{(ER^2)''}{2}\right] \ln\left(\frac{d}{R_0}\right), \tag{4}$$

where R is the radius of the jet, v the cross-sectional average axial fluid velocity, Q the flow rate, ρ the fluid density, g acceleration due to gravity, F_T the tensile force in the jet found from fluid stresses $\pi R^2(\tau_{zz} - \tau_{rr})$, γ the surface tension, σ the surface charge density, ε and ε_0 the dielectric constants of the jet and the ambient air, respectively, E the electric field, K the electrical conductivity, I the current, E_∞ the applied external electric field, d the distance between the nozzle and the collector, and R_0 is the radius of the spinneret, and the primes indicate derivatives with respect to the axial direction, z.

In this work, the continuity and momentum equations are kept as before, but the charge and electric field equations are simplified for the case of low electrical conductivity ($<10^{-10}$ S/m) which is typical for polymer melts [21,22]. From numerical investigations using the model by Feng [13] and parameters from Carroll and Joo [15], we found that as the conductiv-