CAPILLARY FLOW OF CARBONACEOUS MESOPHASE AND ITS STABILITY

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Introduction

As a part of the fiber spinning process, the carbonaceous mesophase flows through the spinnerete capillary, a section of the spinning apparatus which is widely believed to be crucial in determining the final microstructure of the spun fiber [4]. The as-spun carbon fiber can have a variety of microstructures depending on the processing conditions and melt rheology. Some of these structures include: a radial texture where the disks representing the molecular orientation are aligned in the radial direction, possible concentric "onion-skin" textures and a variety of intermediate molecular orientations. Optical observations on both transverse and longitudinal sections of the mesophase pitch samples quenched during flow through capillaries suggest that the radial alignment of molecular "disks" may be unstable depending on the flow processing conditions [3, 1]. The flow-induced texture has often been referred to as the banded or zig-zag microstructure made up of concentric bands with zig-zag layering of the mesophase layers at intermediate angles that alternate from one band to the next. McHugh and Edie [6] recognized that the radial texture of the carbon fiber can be traced to a mathematical solution of Leslie-Ericksen equations for capillary flow, identified by Leslie [5]. More recently, Singh and Rey [7] suggested an adhoc link between these possible fiber microstructures to results of their numerical studies of simple shear flow of a Doi model of discotic liquid crystals. However, a satisfactory mechanism still remains to be identified.

Theoretical Analysis

The present work is directed towards a detailed stability analysis of mesophase pitch capillary flow with the objective of explaining the mechanisms behind generation of flow textures leading to the final fiber microstructure. The mesophase pitch flow is modelled by Leslie-Ericksen continuum equations. The flow Reynolds number based on the capillary diameter is near zero. Neglecting the inertia and gravity terms and with the assumption of incompressibility, the mass and momentum conservation equations reduce to

$$\nabla \cdot \mathbf{v} = 0, \quad \nabla \cdot \mathbf{T} = \nabla p$$

where p is the pressure. A convenient form of the Leslie-Ericksen viscous stress $\mathbf{T}$ and the torque balance is given [2] as

$$\begin{aligned} \mathbf{T} &= \mu_1 \mathbf{n}(\mathbf{n}.\mathbf{D}.\mathbf{n})\mathbf{n} + \mu_2[\mathbf{n}(\mathbf{D}.\mathbf{n}) + (\mathbf{D}.\mathbf{n})\mathbf{n}] \\ &+ \alpha_4 \mathbf{D} + \mu_3(\mathbf{nh} - \mathbf{nn}(\mathbf{h}.\mathbf{n})) + \mu_4(\mathbf{hn} - \mathbf{nn}(\mathbf{h}.\mathbf{n})) \\ \text{and } &\gamma_1(\partial \mathbf{n}/\partial t + (\mathbf{v}.\nabla)\mathbf{n}), = \mathbf{h} \cdot (\mathbf{I} - \mathbf{nn}) + \gamma_1 \boldsymbol{\Omega} \cdot \mathbf{n} \\ &- \gamma_2 \mathbf{D}.\mathbf{n} + \gamma_2 \mathbf{n}(\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{n}) \\ \text{where } &\mathbf{D} = \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^{\mathbf{T}}), \boldsymbol{\Omega} = \frac{1}{2}(\nabla \mathbf{v} - \nabla \mathbf{v}^{\mathbf{T}}) \end{aligned}$$

and the unit vector $\mathbf{n}$ is the director giving the local direction of alignment. The coefficients are defined as $\mu_1 = (\alpha_1\gamma_1 + \gamma_2^2)/\gamma_1$, $\mu_2 = (\alpha_5\gamma_1 - \gamma_2\alpha_2)/\gamma_1$, $\mu_3 = (\alpha_2/\gamma_1)$ and $\mu_4 = (\alpha_3/\gamma_1)$, where the six Leslie viscosities, $\alpha_1, ..., \alpha_6$ satisfy the following thermodynamic restrictions.

$$2\alpha_1 + 3\alpha_4 + 2\alpha_5 + 2\alpha_6 \geq 0, \ \ 2\alpha_4 + \alpha_5 + \alpha_6 \geq 0,$$
$$\alpha_3 \geq \alpha_2, \ 4(\alpha_3 - \alpha_2)(2\alpha_4 + \alpha_5 + \alpha_6) \geq (\alpha_3 + \alpha_2)^2$$

and Parodi's relation, $\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3$ with $\alpha_4 \geq 0$. Also, $\gamma_1 = (\alpha_3 - \alpha_2)$ and $\gamma_2 = (\alpha_2 + \alpha_3)$. For discotics, $\alpha_2 > 0$ and the ratio $\alpha_3/\alpha_2 > 0$ can take values much larger than one. We assume a simple expression for the elastic molecular field, $\mathbf{h} = K\nabla^2\mathbf{n}$.

Base State and Linear Stability

For capillary flow these equations possess the following exact solution describing the radial orientation of the mesophase layers during capillary flow [5]

$$\mathbf{v}^o = (0, 0, \frac{-\triangle P}{L}\frac{1}{2\alpha_4}(R^2 - r^2)), \ \ \mathbf{n}^o = (0, 1, 0)$$

where $(-\triangle P)/L$ is pressure drop per unit length across the capillary and R, the capillary radius. The axial parabolic velocity profile is identical to that for capillary flow of isotropic fluid.

Neglecting dependence on z, the small amplitude disturbances (n'_i, v'_i, p') are assumed to be of the form

$$(n'_i, v'_i, p') = (n_i, v_i, p)(r)\exp^{\iota m\theta + \sigma t}$$

Linearizing the balance equations, substituting for the perturbed variables and non-dimensionalizing, we obtain a set of linear o.d.e.s. To ensure smoothness and boundedness of the physical variables at the capillary centerline, the detailed boundary conditions at $r = 0$ for various values of m are derived in [2]. At the capillary wall, conditions of no-slip velocity and strong director anchoring are enforced. A chebyshev collocation approach is taken to solve the linear stability problem, which is described in details by Didwania [2]. Expressing the perturbation equations in terms of the chebyshev variables at the collocation points and using the specified boundary conditions, we generate a linear system equations which are arranged as

$$L\psi = \sigma N\psi$$

where now $\psi = (v_{rj}, v_{\theta j}, v_{zj}, p_j, n_{rj}, n_{zj})$ denotes the perturbed variables at the collocation points, j. Here L and N are the complex non-hermitian square matrices and the eigenvalue σ gives the dispersion relation

$$\sigma = f(\frac{\alpha_2}{\alpha_4}, \frac{\alpha_3}{\alpha_4}, \frac{\alpha_5}{\alpha_4}, Er, m)$$

with the corresponding eigenvectors yielding the disturbance profile. The process parameter Er refers to an "Ericksen" number, defined as $Er = \frac{-\triangle P}{L}\frac{R^3}{K}$.

Results

Our stability calculations exhibit a Hopf bifurcation implying director tumbling for the full range of Leslie viscosities unlike the well-known exchange of stability that holds for rod-like liquid crystals. For usual high values of process parameter, Er, the flow stability is strongly influenced by the choice of $\frac{\alpha_2}{\alpha_4}, \frac{\alpha_3}{\alpha_4}, \frac{\alpha_5}{\alpha_4}$, implying a very important role of shear viscosity in controlling the director orientation. Non-axisymmetric modes $m \neq 0$ are most unstable, value of m strongly influenced by the viscosity ratios. As the study reveals, a wide variety of director orientations are possible depending on the pitch rheology represented by Leslie viscosities which in turn depend on processing conditions like temperature, flow rate, etc. The linearized director field disturbances is reminiscent of the banded or zigzag microstructure widely observed in the "near rim" zone of a typical highly textured carbon fiber spun from mesophase.

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