THE DEVELOPMENT OF ORIENTATION IN MESOPHASE PITCH DURING FIBER FORMATION

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Introduction

Because of their extremely high strength, stiffness, and thermal conductivity, composites reinforced with mesophase pitch-based carbon fibers are ideally suited for structural applications where the rapid dissipation of heat is important. Presently, carbon fibers are produced commercially by the high-temperature carbonization of polyacrylonitrile (PAN), isotropic pitch, and mesophase pitch precursors. Since the thermal conductivity of carbon fibers is a result of their graphite-like crystallinity, it is desirable to employ a precursor that produces the greatest graphitic order. This makes mesophase pitch, a liquid-crystalline material which tends to orient in a shear field (e.g., during extrusion), a particularly attractive precursor. This orientation developed during the extrusion of mesophase is enhanced during drawdown and perfected during heat treatment, resulting in the formation of large, crystalline domains that extend essentially parallel to the fiber axis. Because of this peculiarity, carbon fibers produced from mesophase pitch can exhibit outstanding thermal conductivity.

It has been shown that, in addition to the longitudinal orientation (which may be developed during fiber drawdown), the transverse texture also has a significant impact on the thermal properties of mesophase pitch-based carbon fibers. This transverse microstructure seems to be solely dependent on flow during extrusion; i.e., the drawdown and subsequent heat treatment apparently do not greatly affect fiber texture. For this reason, if the structural perfection and ultimately the properties of mesophase pitch-based carbon fibers are to be optimized, there has been a need for a more fundamental understanding of the unusual flow behavior of mesophase pitch. Specifically, a major part of this work has involved an effort to model the flow and orientation of mesophase pitch through channels of a given cross-section and to compare the predicted orientation patterns with experimental evidence. Bearing in mind that the ultimate goal is to improve fiber thermal conductivity, the results of this approach have been used to modify spinnerette design, in order to precisely control fiber texture. Improvements in the quality of the as-spun fiber can enhance its "graphitizability," substantially reducing the cost of heat treatment.

Theory

The modeling work utilized the theory developed by Leslie [1] and Ericksen [2] which describes the fluid mechanics of nematic liquid crystals. The orientation is described by a unit vector called the director, $\boldsymbol{n}$, which points in the direction around which the molecules possess rotational symmetry. The conservation of mass, linear momentum, and angular momentum in this model are

$$(\nabla \bullet \boldsymbol{v}) = 0 \ ,$$

$$\rho \frac{\partial \boldsymbol{v}}{\partial t} = -\rho(\boldsymbol{v} \bullet \nabla)\boldsymbol{v} - \nabla P + [\nabla \bullet \boldsymbol{\tau}] \ ,$$

$$\boldsymbol{\Gamma}_{\text{elas}} + \boldsymbol{\Gamma}_{\text{visc}} = 0 \ .$$

where $\boldsymbol{v}$ is the fluid velocity, ρ is the density, P is the pressure, $\boldsymbol{\tau}$ is the viscous stress tensor, $\boldsymbol{\Gamma}_{\text{visc}}$ is the viscous torque and $\boldsymbol{\Gamma}_{\text{elas}}$ is the elastic torque. The viscous stress tensor is given by

$$\boldsymbol{\tau} = \alpha_1 \boldsymbol{n}(\boldsymbol{n} \bullet [\mathbf{A} \bullet \boldsymbol{n}])\boldsymbol{n} + \alpha_2 \boldsymbol{n} \boldsymbol{N} + \alpha_3 \boldsymbol{N} \boldsymbol{n} + \alpha_4 \mathbf{A} + \alpha_5 \boldsymbol{n}[\boldsymbol{n} \bullet \mathbf{A}] + \alpha_6 [\boldsymbol{n} \bullet \mathbf{A}]\boldsymbol{n} \ ,$$

where α_i are the Leslie viscosity coefficients, while **A** is the rate of deformation tensor and $\boldsymbol{N}$ is the director motion vector given by

$$\mathbf{A} = \frac{1}{2}([\nabla \boldsymbol{v}] + [\nabla \boldsymbol{v}]^T) \ ,$$

$$\boldsymbol{N} = \frac{\partial \boldsymbol{n}}{\partial t} + (\boldsymbol{v} \bullet \nabla)\boldsymbol{n} - \frac{1}{2}[[\nabla \times \boldsymbol{v}] \times \boldsymbol{n}] \ .$$

The elastic torque is defined as

$$\boldsymbol{\Gamma}_{\text{elas}} = [\boldsymbol{n} \times \boldsymbol{h}] \ ,$$

where $\boldsymbol{h}$ is the molecular field, which is given by

$$\boldsymbol{h} = K[\nabla^2 \boldsymbol{n}] \ ,$$

where K is an average elastic material constant. The viscous torque is described by a constitutive relation, or

$$\boldsymbol{\Gamma}_{\text{visc}} = -(\alpha_3 - \alpha_2)[\boldsymbol{n} \times \boldsymbol{N}] - (\alpha_2 + \alpha_3)[\boldsymbol{n} \times [\mathbf{A} \bullet \boldsymbol{n}]] \ .$$

Results

When the above equations are applied to the situation of capillary flow, the liquid crystal flow model was found to predict the development of a radial texture commonly observed in circular mesophase pitch-based carbon fibers (see Figure 1). In this analysis, the axial orientation was assumed to be perfect, and the transverse orientation was determined as the equilibrium where the torques on the molecules sum to zero [3].

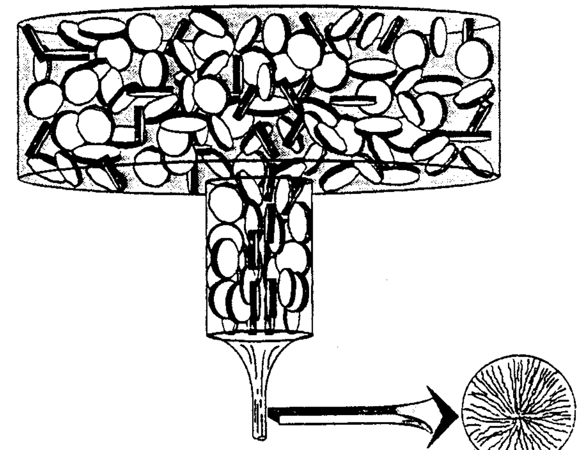

Figure 1. Origin of radial texture in mesophase fibers.

The model also was able to accurately represent the "line-origin" texture of mesophase pitch fibers produced with a ribbon shape (which seems to be more conducive to developing high thermal conductivity [4]), as shown in Figure 2. Again, in this case, the axial orientation was assumed to be perfectly developed.

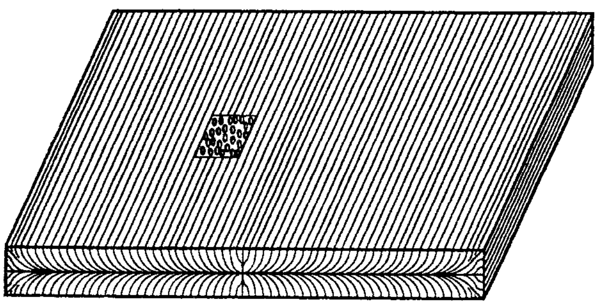

Figure 2. Orientation of mesophase pitch in a rectangular channel.

Furthermore, this connection between the predicted orientation and fiber texture was supported by optical photographs of a heat-soaked and a naphthalene-based mesophase quenched during flow (in a manner similar to the technique described by Fathollahi *et al.* [5]) through a rectangular capillary and viewed between crossed polarizers. These results provide evidence that the structure of mesophase pitch-based carbon fibers is created within the spinnerette capillaries. Results will be presented which demonstrate this.

In a related study, the effect of spinnerette capillary entrance geometry on fiber structure and properties was investigated. A rectangular capillary spinnerette was constructed with a tapered channel entrance. Upon graphitization to 2400°C, fibers produced using this spinnerette developed electrical resistivities of 2.1 $\mu\Omega\cdot$m, as compared with a value of 4.5 $\mu\Omega$m of fibers processed under similar conditions using a spinnerette with a flat capillary entrance region. These results point toward the critical importance of spinnerette design on fiber properties, due to the viscoelastic nature of mesophase pitch.

Conclusion

This work represents the first successful application of liquid crystal theory to carbon fiber technology. Unfortunately, understanding of the physics of liquid crystals and carbon fiber technology has developed independently over the past few decades, and each field has its own nomenclature and priorities. As a result, there are very few individuals who have a thorough understanding of liquid crystal physics *and* carbon fiber processing.

In the past, experimental verification of the Leslie-Ericksen model has been limited to the characterization of a small number of laboratory-prepared nematic compounds which are of little practical value. Conversely, the term "mesophase" has been applied liberally to certain pitch-derived materials, with little regard as to whether they behave dynamically as liquid crystals. Therefore, perhaps the most important contribution of this work is the synthesis of these two technologies and the resulting explanation for the origin of mesophase fiber texture. It is hoped that this work provides the impetus for improvements in spinnerette design, because it seems certain that advances in this particular area offer the most cost-effective route to further enhance the properties of mesophase pitch-based carbon fibers.

References

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