

DRAWING OF COMPOUND POLYMERIC FIBERS

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Abstract

A two-dimensional model of the drawing of slender compound plastic fibers that employs a Newtonian rheology for both the core and the cladding and accounts for the molecular orientation and crystallization is presented. The model is based on the use of asymptotic expansions in power series of the slenderness ratio and two-dimensional resolution of the temperature, molecular orientation and crystallization fields. It is shown that the polymer molecules are almost fully oriented near the die exit where the strain rate and the fiber's contraction are largest and that the degree of crystallization and the temperature exhibit large radial variations at the take-up roller where the fiber is collected. The deficiencies of the model are discussed and some suggestions for improvement are provided.

1 Introduction

Compound or bi-component fibers consist of a core and a cladding of, in general, different properties that are manufactured by either extrusion from a melt or by first heating a preform to above its melting temperature and then extruding the resulting melt through an annular die. Compound fibers are frequently used in textiles, optics (e.g., plastic optical fibers), composite materials, membranes, etc. In some of these fibers, the cladding consists of a material that serves as a wave guide in signal processing applications, e.g., in optics, protects the core, e.g., in textiles and composites, or has better surface properties than the core.

The properties of compound plastic fibers manufactured by heating the polymer to above its melting temperature and then extruding or drawing the melt while simultaneously cooling it, depend on the processing conditions and the molecular structure of the polymers; polymers that are unable to crystallize upon cooling below their glass transition temperature, form amorphous solids which can exhibit strong anisotropy, whereas polymers that are able to crystallize form semi-crystalline fibers. The degree of crystallization depends on the processing conditions, i.e., drawing ratio and cooling, as well as on the rheology and molecular structure, and is, therefore, affected by the flow and the temperature fields, i.e., the crystallization depends on the flow and thermal fields.

Most of the research performed to-date on the drawing of compound fibers has been concerned with melt spinning processes of amorphous materials and slender fibers for which one can easily derive one-dimensional models by using either Taylor's series expansions in the radial direction or by averaging the conservation equations of mass, linear momentum and energy across the fiber; alternatively, one can use asymptotic methods based on the slenderness ratio to derive one-dimensional equations at leading-order in the slenderness ratio.

The validity of such an asymptotic derivation requires that the heat exchanges with the surroundings be sufficiently small, i.e., on the order of the square of the slenderness ratio, and such assumption, in turn, yields a one-dimensional equation for the temperature of the compound fiber at leading-order, i.e., at leading-order, the temperature of the cladding is equal to that of the core and the temperature is uniform across the fiber. Although one-dimensional models of compound fibers have been employed in the past to study, for example, the high-speed melt spinning of amorphous bi-component fibers consisting of poly (ethylene terephthalate) (PET) in the core and polypropylene (PP) in the cladding and Newtonian and upper-convected Maxwell rheologies [1] as well as the drawing of semi-crystalline compound fibers of Newtonian fluids at moderate speeds [2], these models do not account for the radial variations of temperature, molecular orientation and degree of crystallization across the compound fiber, even though these variations are of paramount importance in determining the mechanical, optical, chemical, etc., properties of compound plastic fibers.

Attempts to develop a fully two-dimensional model of the drawing of compound fibers must face the fact that the conservation equations of mass, linear momentum and energy are strongly coupled through the pressure field and the dependence of the properties on temperature, molecular orientation and crystallization; in addition, the core-cladding and the core-surrounding medium interfaces must be determined in the solution procedure. At these interfaces, the velocity, temperature, tangential stresses and normal heat flux are continuous, while the jump in normal stresses is balanced by surface tension; for semi-crystalline fibers, the interface conditions for the molecular orientation and the degree of crystallization are not known although one suspects that these interfaces are of the diffuse type and there is reptation of the polymer molecules there. This implies that a two-dimensional model of the drawing of compound fibers will require a time-consuming numerical solution and will not be competitive with one-dimensional ones. For this reason, in this paper, a hybrid two-dimensional model of compound plastic fibers is presented. The model is analogous to the hybrid one developed by the author and co-workers [3], except that employs an order parameter for the molecular orientation rather than a tensor and is based on the assumption that the molecular orientation tensor is proportional to the leading-order velocity gradient (tensor) for slender compound fibers.

Since the paper is mainly a review of two-dimensional models of the drawing of compound polymer fibers, a brief description of the physics and mathematics is presented in Section 2 where the limitations of the models are also discussed. Some sample results are described in Section 3 which also contains comparisons between the results of one- and two-dimensional models. A final section on Conclusions summarizes the most important findings reported in the paper.

2 Model formulation

As stated in the previous section, the model for the drawing of compound plastic fibers presented here is a hybrid one; it assumes that the polymers that compose the cladding and core are incompressible and that their rheologies consist of Newtonian and polymeric parts. The dynamic viscosities of the Newtonian stress tensor depend on the temperature through an Arrhenius expression and the degree of crystallization through an expression proposed by Ziabicki [4-6]. For the modeling of the polymeric contribution to the stress tensor, we have assumed that polymer molecules that form liquid-crystalline phases in solution generally have rigid backbones and consequently have rod-like shapes and that the solution of rod-like polymers behaves as an ensemble of rigid dumbbells suspended in a Newtonian solvent.

Moreover, by assuming that the polymeric contribution to the stress tensor depends on the molecular orientation tensor and modeling the latter by means of a probability density function for the molecular orientation vector and by taking moments of the probability density function and modeling the fourth-order moments in terms of second-order ones, one can derive a partial differential equation for the molecular orientation tensor which depends on the flow strain rate and the relaxation of the molecular chains [7].

The partial differential equation for the molecular orientation tensor contains a source term that depends on the velocity gradient and a sink one that hinders the molecular orientation and depends on the temperature, velocity and molecular orientation, although it should also include some dependence on the degree of crystallization. The orientation tensor has nine components but, by assuming symmetry and considering slender fibers, it can be shown that this tensor is diagonal at leading-order in an asymptotic expansion for slender fibers. Moreover, since the tensor is traceless, it has only two independent components [2, 3]. The velocity gradient for slender fibers is also diagonal at leading-order for slender fibers.

If the molecular orientation tensor is assumed to be proportional to the velocity gradient for slender fibers, it becomes a diagonal one and depends only on one parameter which is referred to as the order parameter. Furthermore, this assumption implies that, at leading-order in the slenderness ratio, the polymeric contribution to the stress tensor is proportional to the Newtonian one and, therefore, the total stress tensor is proportional to the strain rate one with an effective dynamic viscosity that is the sum of two terms: the Newtonian one and the one associated with the molecular orientation that depends on the temperature and the order parameter for the polymer orientation. This implies that the contribution of the molecular orientation to the effective dynamic viscosity is additive while the effects of the temperature and crystallization are multiplicative.

The crystallization of the polymer molecules has been modeled according to the Avrami-Kolmogorov (thermal) kinetic formulation [8,9] modified by taking into account the coupling between the degree of crystallization and the polymer orientation [4] and relating the elongational viscosity of the melt to the degree of crystallization [5,6]. This implies that the crystallization of the polymer molecules is governed by two-dimensional first-order partial differential equations whose solution can be determined by specifying two boundary conditions one each along the axial and radial directions; a similar comment applies to the molecular orientation tensor or the molecular order parameter employed here. As a consequence, the degree of crystallization and the molecular orientation may not be continuous at the core-cladding interface. In order to have continuity at those interfaces, it is required to include diffusive phenomena in the radial direction there, e.g., molecular reptation, Brownian motion, etc.

In the formulation presented here, the radial and axial coordinates were non-dimensionalized with respect to the maximum radius of the fiber and the axial distance between the maximum swell cross-section and the take-up roller; this distance was assumed to be much larger than the radius of the fiber at the maximum swell cross-section, so that the fiber is slender. The axial velocity component was non-dimensionalized with respect to a constant reference value at the die's exit, whereas the continuity equation provides the value of the reference value for the radial velocity component which is smaller than the axial one. The temperature was normalized with respect to the melting one and a lubrication or long-wave-length approximation was used to scale the pressure. Gravitational effects were included while capillary ones were neglected because surface tension effects are usually small in fiber drawing. Also neglected was the drag force on the outer surface of the cladding because we

are here mainly concerned with moderate drawing speeds; drag effects are important at high draw ratios.

At the outer surface of the cladding, there are heat exchanges by convection and radiation between the fiber and the surrounding; these effects can be included into only one by employing a nonlinear heat film transfer coefficient that depends on the temperature. For Biot numbers on the order of or larger than unity, it is not possible to perform an asymptotic analysis of the governing equations in power series of the slenderness ratio. For such an analysis to be possible, it is required that the Biot number be on the order of the square of the slenderness ratio, i.e., the Biot number must be small. Under these conditions, the boundary conditions for the energy equation are of the adiabatic type at leading-order and give rise to a one-dimensional model for the axial velocity component and temperature fields which have to be determined at second-order in the asymptotic expansion. The temperature field may include axial conduction, but this term can be neglected at high thermal Péclet numbers.

The assumption that the Biot number be sufficiently small in order that the axial velocity and temperature fields be approximated by one-dimensional equations in drawing processes of slender fibers has not been strongly emphasized in the past and is a serious one; in fact, most one-dimensional models of these processes use appropriately fitted heat transfer correlations in order to predict accurately the fiber geometry and the stresses. This assumption also yields a radial velocity component that depends linearly on the radial coordinate and is directed towards the fiber's symmetry axis.

In order to account for the radial variations of temperature, molecular orientation and degree of crystallization in the drawing of semi-crystalline compound fibers, we have used a hybrid two-dimensional model whereby the axial and radial velocity components and the fiber's radius are those obtained from an asymptotic analysis of slender fibers at low Biot numbers, i.e., small heat transfer exchanges at the cladding's outer surface, and are governed by one-dimensional equations, and two-dimensional equations for the crystallization, molecular orientation and temperature fields. Such a hybrid model is much simpler than a fully two-dimensional formulation of the problem and reduces to existing one-dimensional formulations for small heat exchanges; it also avoids the numerical problems that may appear in fully two-dimensional formulations where the core-cladding and cladding-surrounding medium interfaces must be determined in the solution. However, since the effective viscosity that appears in the one-dimensional axial momentum equation depends on the two-dimensional temperature, molecular orientation and degree of crystallization fields, it is necessary to use its cross-sectional averaged value and this renders the problem into an integro-differential boundary-value one. It must also be noted that the hybrid model presented here is also applicable to study the drawing of amorphous compound fibers by simply disregarding the equations for the molecular orientation and the crystallization.

In order to solve the one-dimensional equations for the two radii of the compound fiber and the axial velocity component and the two-dimensional equations for the temperature, molecular orientation and degree of crystallization, the curvilinear geometry of the compound fiber was mapped into two rectangles one each for the core and the cladding, and the governing equations in the computational domain were solved by means of finite difference equations as follows. First-order accurate finite differences were used to discretize the advection terms in the axial and radial directions, central differences were employed for the discretization of the diffusion terms in the radial direction, and the cross-sectional averaged values of the effective dynamic viscosity were evaluated by means of a second-order accurate trapezoidal rule.

Unequally-spaced grids have been employed in the axial and radial directions; in the axial one, the grid points were concentrated near the maximum swell region where the strain rate and the compound fiber's contraction are largest, whereas, in the radial direction, the grid points were concentrated at the core-cladding interface and at the cladding's outer surface where the largest gradients of temperature are expected. The system of nonlinear algebraic equations that result from the finite difference discretization of the governing equations was solved iteratively starting from the analytical solution corresponding to a compound fiber at very low Reynolds numbers and uniform temperature, molecular orientation and crystallization fields until convergence of all the dependent variables was achieved.

3 Results

The number of non-dimensional parameters that govern the drawing of semi-crystalline compound plastic fibers is very large and includes the draw ratio, i.e., the ratio of the velocity at the take-up roller where the fiber is collected to that at the die's exit, the slenderness ratio, the volumetric flow rate ratio, the Reynolds, Froude, capillary and Nusselt numbers, the core-to-cladding density, viscosity, thermal conductivity and heat capacity ratios, etc. In addition, these processes depend on the properties and temperature of the surrounding media, the Zel'dovich numbers associated with the dynamic viscosity law, the melting temperatures of the polymers that compose the core and cladding, etc. A study of the effects of all of these non-dimensional groups on the drawing of semi-crystalline compound plastic fibers would be very demanding. Therefore, based on our previous experience with one-dimensional models [2], we have only considered a small set of parameters and assessed their influence on the drawing process. Moreover, since the results obtained with the molecular order parameter formulation presented above are analogous to those that have been obtained with a two-parameter molecular orientation tensor [3], we will limit our presentation to a discussion of the results.

Numerical studies indicate that the largest initial cooling of the compound fiber occurs at the cladding's outer surface and this causes a dramatic increase of the effective dynamic viscosity there. Although the dynamic viscosity is a function of the temperature, degree of crystallization and molecular orientation, it has been observed that the contribution of the latter are much smaller than that due to the increase in viscosity as the temperature decreases; this indicates that, for the conditions considered here, the polymeric contribution to the total stress tensor is smaller than that of the Newtonian one. These results are in accord with the dependence of the dynamic viscosity on temperature used in this study where it has been assumed that the dependence of the dynamic viscosity on temperature follows an Arrhenius law. It has also been observed that the contribution of the crystallization to the stress tensor is much smaller than that of the temperature.

The numerical studies performed with the hybrid model presented here also indicate that the polymer molecules get fully oriented near the maximum swell cross-section where the strain rate and the compound fiber's contraction are largest. According to the molecular orientation model presented here, this implies that the source term of the partial differential equation for the orientation tensor is larger than the sink term; however, once the fiber solidifies the source term becomes nil and the sink one may cause a (clearly unphysical) decrease of the molecular orientation. In order to overcome this deficiency, one could modify the sink term or assume that the relaxation time that appears in that term tends to infinity as solidification is approached.

It has also been observed that the degree of crystallization increases along the compound fiber but it never achieves its ultimate value [4-6]. Moreover, in the studies reported here, thermal

effects on crystallization were found to dominate over flow-induced ones. If this were also the case at high drawing speeds, it could be concluded that the hybrid model presented here would not be able to predict the neck-in phenomenon which is characterized by a rapid localized contraction of the fiber.

When the radial profiles of the molecular orientation order parameter and the degree of crystallization are uniform at the maximum swell cross-section, they remain uniform but their values vary with the axial distance along the fiber; however, they may be different if their values at the maximum swell cross-section are different. This implies that the molecular orientation and crystallization may not be continuous at the core-cladding interface and this is in accord with the hyperbolic equations for these two variables. This, in turn, implies that the dynamic viscosity is not continuous at the core-cladding interface.

According to the rheology employed in this study, a decrease in temperature results in an (exponential) increase of the effective dynamic viscosity; this, in turn, implies that the solidification of the compound plastic fibers considered here is associated with the exponential increase of the viscosity as the temperature decreases, although it is also influenced (but to a smaller degree) by the crystallization and the molecular orientation.

In order to increase the heat transfer between the fiber and its surrounding medium, both parallel and perpendicular flows of cooling air may be employed; this causes an increase in the Biot number. It has been observed that the contraction of the compound fiber increases as the Biot number is increased on account of the increase in heat transfer losses, the temperature drop at the cladding's outer surface and the increase in the dynamic viscosity; therefore, the solidification of the fiber occurs closer to the maximum swell cross-section as the Biot number is increased. The magnitude of the radial velocity component and the strain rate at the maximum swell cross-section also increase as the Biot number is increased.

The molecular orientation also increases and occurs closer to the maximum swell cross-section as the Biot number is increased; however, it has been observed that the crystallization model presented here predicts that the degree of crystallization decreases as the Biot number is increased. This result is consistent with the modified Avrami-Kolmogorov formulation for crystallization presented here, for the residence time near the maximum swell cross-section decreases as the Biot number is increased, whereas the rate of crystallization presented here depends linearly on the degree of crystallization and exponentially on the degree of molecular orientation mainly; therefore, the rate of crystallization is influenced indirectly by the temperature whereas the axial velocity component is affected directly by the temperature through the dynamic viscosity.

It has been found that the most important parameters that affect the drawing of compound plastic fibers are those that either are affected directly by or influence the energy equation, i.e., the heat transfer losses, the dynamic viscosity, i.e., its pre-exponential factor and activation energy, and the thermal conductivity of the cladding. Moreover, it has been observed that the profile of the axial velocity component as a function of the axial distance measured from the maximum swell cross-section is a monotonously increasing, one-signed curvature function until the fiber solidifies, for large Biot numbers, but may have a two-signed curvature at low Biot numbers. Again, this is related to the fact that the fiber's contraction near the maximum swell cross-section increases as the Biot number is increased.

Since, in the model propose here, solidification is associated with a large increase in dynamic viscosity as the temperature decreases and the dynamic viscosity dependence on temperature

is stronger than those on the degree of crystallization and the molecular orientation, it has been found that crystallization is mainly controlled by the thermal Avrami-Kolmogorov kinetics formulation and that flow-induced crystallization is small.

The hybrid model indicates that substantial temperature non-uniformities in the radial direction exist even at moderately low Biot numbers. These non-uniformities affect the degree of crystallization and may have great effects on the properties of compound fibers. On the other hand, good agreement between the predictions of the two-dimensional model presented here and those of a one-dimensional one was found for slender fibers at low Biot numbers; at higher Biot numbers, the cross-sectional averaged quantities of the two-dimensional model were found to be in qualitative agreement with those of one-dimensional models although major differences have been observed in the fiber's contraction near the maximum swell cross-section and in the dependence of the temperature on axial distance along the fiber. In particular, the one-dimensional model predicts a one-signed axial velocity profile while the predictions of the two-dimensional one depend on the Biot number.

The modeling of the drawing of compound plastic fibers presented here employs a single-phase one-component formulation and does not include the effects of the latent heat of solidification; these effects are usually small except near the solidification cross-section. The formulation does not include the swelling phenomenon that may occur in drawing polymers, nor is it valid for predicting the melt flow within the die. Moreover, as discussed above, the solidification occurs due to the large increase of the dynamic viscosity as the temperature decreases and flow-induced crystallization has been found to be much smaller than the thermally induced one; therefore, the model is not strictly applicable to high-speed drawing of semi-crystalline polymers which may undergo a localized sharp contraction downstream from the solidification cross-section.

Improvements to the model presented here include a two-phase formulation for the amorphous and crystalline phases, a polymeric contribution to the stress tensor that includes visco-elastic terms and their corresponding relaxation times (which may depend on the temperature and the degrees of crystallization and molecular orientation), a modified crystallization model that accounts not only for the molecular orientation and the crystallization as the model presented here, but also for the temperature field, and models for the crystallization and molecular orientation at the core-cladding interface where the model presented here shows discontinuities due to the hyperbolic equations that govern these two variables.

4 Conclusions

A hybrid two-dimensional model for the drawing of compound polymer fibers that employs a Newtonian rheology for the melt and uses a polymeric contribution to the stress tensor that depends on the molecular orientation, has been presented. The model employs a transport equation for the molecular orientation tensor based on the assumption that the polymer molecules have rod-like shapes and that the solution of rod-like polymers behaves as an ensemble of rigid dumbbells suspended in a Newtonian solvent, while the solidification and crystallization of the polymers have been modeled by means of a thermal Avrami-Kolmogorov formulation modified to account for the effect of crystallization on the dynamic viscosity.

It has been found that the most important parameters that affect the drawing of compound polymer fibers are those affected by the temperature, i.e., the dynamic viscosity, the heat transfer losses, and the thermal conductivity of the cladding. At large Biot numbers, the axial

velocity profile is a one-signed curvature, monotonously increasing function of the axial distance along the fiber, whereas, at low Biot numbers, it may have a two-signed curvature. The fiber solidification was found to be due to the large increase of the dynamic viscosity as the temperature decreases and very little dependent on the degrees of crystallization and molecular orientation.

It has been shown that almost full molecular orientation is obtained near the maximum swell cross-section where the strain rate and the fiber's contraction are largest, while the degree of crystallization increases along the fiber but it never reaches its ultimate value. The degree of crystallization was also found to decrease as the heat transfer losses increase due to the large contraction of the fiber near the maximum swell cross-section and the decrease of the residence time, so that most crystallization is of the thermal rather than of the flow-induced type.

Large radial variations across the fiber have been observed at the roller take-up location where the fiber is collected. These variations result in the formation of an annular shell at the cladding's outer surface and affect the properties of compound fibers.

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