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Polymer Crystallization in Complex Conditions. Towards More Realistic Modelling of Industrial Processes

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SUMMARY: Crystallization plays an important role in processing many industrial polymers. Crystallinity controls mechanical and sorptional properties of solid materials and strongly affects rheological properties of polymer melts and solutions. Therefore, realistic modeling of technological processes involving crystallizable polymers (melt spinning, film blowing, injection molding, etc.) requires that crystallization in the course of processing is taken into account. In contrast to idealized laboratory conditions usually applied in academic studies, crystallization in processing conditions covers wide range of rapidly changing temperatures and pressures. Simple models of non-isothermal, and stress-induced crystallization kinetics are discussed. Consideration of crystallization in the computer model of melt spinning reveals new effects, absent in earlier models, in which crystallization was ignored.

1. Introduction

Computer simulation became a routine technique in many fields of polymer science and technology, replacing expensive and time-consuming experiments. The success of modelling, however, largely depends on specific assumptions about material behavior. Results of simulation are never better than the input information used for solving, however sophisticated, dynamic equations. Optimization of injection molding, fiber and film formation, and other processes provides motivation for theoretical and experimental studies of the development of polymer structure in conditions not encountered in academic laboratories. We will concentrate on the effects of polymer crystallization and will discuss fiber formation (melt-spinning), as an example of an industrial process.

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2. Mathematical model of an industrial process

Dynamics of an industrial process are described by a set of ***conservation equations***, solved together with ***constitutive equations***, describing properties of the material, ***equations of evolution*** of structure and material properties, as well as appropriate ***boundary conditions*** (Figure 1). The basic conservation equations concern conservation of mass, momentum and energy. Constitutive equations include the relation between stress tensor and history of relative deformation, as well as material characteristics. An important constitutive equation concerns internal energy, U, depending on temperature and phase composition. As evident in Figure 1 all equations describing dynamics of an industrial process are coupled. In this coupling, an essential role is played by crystallinity.

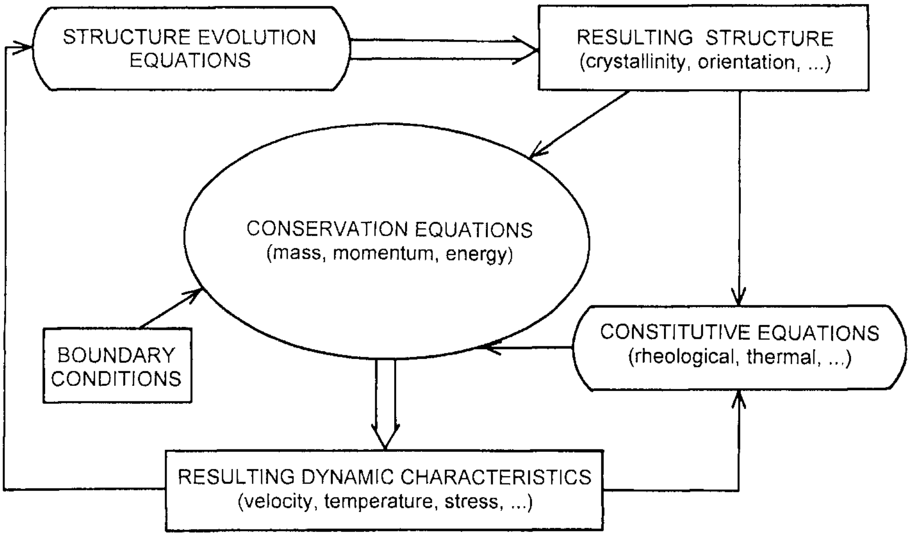

Figure 1. Equations describing a dynamic process with variable structure (schematic).

Crystallinity, x, (and other structural features) affects such material properties as density (appearing in all conservation equations), and specific heat. More important, however, is effect of crystallinity on the rheological properties of the polymer, appearing in the constitutive equation for stress. Crystallization can dramatically modify dynamics of polymer deformation. To make the model realistic, one has to consider evolution of structure (i.e. development of crystallinity) in time. Crystallization rate, $\dot{x}$, depends on the progress of phase transformation, x, as well as on the history of temperature, stress, and other conditions.

3. The kinetics of polymer crystallization

The most popular treatment of crystallization kinetics is based on the stochastic model developed independently by Kolmogoroff [1], Avrami [2], Evans [3] and Johnson & Mehl [4]. The KAE theory considers spontaneous formation of crystal nuclei (nucleation) and their subsequent growth in *n* dimensions, resulting in the time-dependent degree of transformation (degree of crystallinity), x(t)

$$x(t) = 1 - exp\left[-E(t)\right] \tag{1}$$

where

$$E(t) = \text{const.} \int_0^t \dot{N}(s)ds \left[\int_s^t G(z)dz\right]^n ; \quad E \in (0,\infty) \tag{2}$$

is a fraction of space covered by „phantom crystals", and $\dot{N}$, and G represent, respectively, nucleation and growth rates. Many phantom crystals can occupy the same physical space, which admits E values higher than unity. In steady-state, isothermal conditions where nucleation and growth rates are constants, Eq.(2) reduces to the simple form

$$E(t) = K_m t^m \tag{3}$$

where K_m (*Avrami constant*) and *m* (*Avrami exponent*) are material characteristics.

Nucleation and growth rates are described by thermodynamic models taking into account molecular characteristics of crystalline aggregates and their mode of growth (cf. refs. [5-7]). The thermodynamic models give physical insight into the mechanisms of polymer crystallization, and can explain effects specific to polymer crystallization, like molecular symmetry and flexibility, selective crystallization of oriented molecules, effects of external fields, etc. [8]. The thermodynamic models, however, usually derived for isothermal, steady-state conditions close to thermodynamic equilibrium, cannot quantitatively describe processes occuring in industrial conditions. Also, reliable measurements of nucleation and growth rates are not available, and cannot fill the gap. Therefore, for the description of industrial processes, along with the development of fundamental, thermodynamic theories, one has to introduce simplified, semi-empirical crystallization models, covering wide range of conditions and based on material characteristics subject to direct measurement.

4. Approximate models of non-isothermal crystallization

The approximate models of non-isothermal crystallization start with the Kolmogoroff-Avrami-Evans formalism. Since separate determination of nucleation and growth rates in Eq.(2) is very difficult (if possible), two different functions, $\dot{N}(t)$ and $G(t)$ are replaced by a single, crystallization rate function K(t). Early models of non-isothermal crystallization kinetics [9-11] were based on the assumption that functions $\dot{N}(t)$ and $G(t)$ are proportional to each other. This ***isokinetic*** assumption yields modified Kolmogoroff-Avrami-Evans equation in the form

$$E(t) = ln\left[\frac{1}{1 - x(t)}\right] \cong \left[\int_0^t K(t')dt'\right]^m \tag{4}$$

In isothermal conditions, K reduces to the „Avrami constant", K_m. The crystallization rate function, K(t), can be obtained from experiments and provides the key characteristic of the model. The exponent, *m*, related to nucleation mechanism and dimensionality of growth has to be evaluated from additional sources of information.

In isothermal conditions, K in Eq. (4) is a constant, dependent on temperature, stress, and other conditions. In industrial processes, external conditions change rapidly. E.g. in melt spinning, local cooling rate may reach 10^3-10^4 K/sec. Early models of non-isothermal crystallization [9-11], considered crystallization as a ***quasi-static*** process in which crystallization rate followed variable external conditions

$$K(t) = K[T(t),\ \mathbf{T}(t),\ \ldots] \tag{5}$$

but did not depend explicitly on time or rates of change. The quasi-static model appeared to be successful in semi-quantitative description of processes with slowly changing conditions.

For real processes, a more general model has been proposed [12]. The model introduces two physical mechanisms absent in isothermal, or quasi-static models: athermal nucleation, and relaxation.

Crystallization rate is assumed as resulting from two nucleation mechanisms: thermal and athermal.

$$K(t) = K_{th}(t) + K_{ath}(t) = K_{th}(t)\left[1 + \frac{\dot{N}_{ath}}{\dot{N}_{th}}\right]^{\mu} \qquad (6)$$

In a system with cluster size distribution, ρ(v), ***nucleation rate***, i.e. the rate of production of stable nuclei, results from differentiation of the integral

$$\dot{N}(t) \equiv \frac{d}{dt}\int_{v^*}^{\infty}\rho(v)dv = N_0\left[\int_{v^*}^{\infty}\frac{\partial\rho}{\partial t}dv - \frac{dv^*}{dt}\rho(v^*)\right] \qquad (7)$$

and after simple transformations, yields two components

$$\dot{N}(t) = \dot{N}_{th} + \dot{N}_{ath} = -N_0\left[j_{gr}(v^*) + \rho(v^*)\frac{dv^*}{dt}\right] \qquad (8)$$

Thermal nucleation consists in the growth of small, unstable clusters to the critical size, v*. Thermal nucleation rate, $\dot{N}_{th}$, is proportional to the flux of clusters passing over a potential barrier at v = v* on the way to stability. The other mechanism, ***athermal nucleation***, has been proposed by Hollomon, Fisher and Turnbull [13] and further analyzed by Ziabicki [14]. In variable conditions, clusters unstable in the original conditions, may become stable when the conditions are changed. Athermal nucleation rate is proportional to the rate with which the critical cluster volume, v*, changes in time because of changing external conditions. Consequently, it is proportional to the ***rate of change*** of external conditions (temperature, T, tensile stress, Δp, etc.)

$$\dot{N}_{ath} \propto \left(\frac{dv^*}{dt}\right) \propto \left[\frac{\partial v^*}{\partial T}\frac{dT}{dt} + \frac{\partial v^*}{\partial \Delta p}\frac{d\Delta p}{dt} + \ldots\right] \qquad (9)$$

In variable conditions, thermal nucleation (and thermal nucleation-based crystallization rate) should be considered as a ***relaxation process.*** In a single-relaxation-time approximation

$$\frac{dK_{th}}{dt} = \frac{K_{st} - K_{th}(t)}{\tau} \tag{10}$$

where steady-state crystallization rate, K_{st}, and „relaxation time", τ, are functions of instantaneous conditions, T(t), $\Delta p(t)$, etc.Because of relaxation, crystallization rate lags behind changing external conditions. The nature of this effect is associated with limited molecular mobility. Crystal nucleation and crystal growth are realized through molecular motions which, especially in polymers, are rather slow.

Combination of Eqs. (6) and (10) yields total crystallization rate in the form

$$K(t) = \left[1 + \frac{\dot{N}_{ath}}{\dot{N}_{th}}\right]^{\mu} \left[e^{-\xi} \int_0^{\xi(t)} e^{\xi} K_{st}(\xi)\, d\xi\right] = \left[1 + f\left(T, \dot{T}, \Delta p, \Delta \dot{p}, \ldots\right)\right] \left[e^{-\xi} \int_0^{\xi(t)} e^{\xi} K_{st}(\xi)\, d\xi\right] \tag{11}$$

where μ is a constant dependent on the mechanism of nucleation and growth. If the growth rate in (*m-1*) dimensions is combined with athermal nucleation, μ reduces to *1/m*. The athermal function, f, is directly proportional to the ***rates of change*** ($\dot{T}$, $\Delta\dot{p}$, ... etc.), and ξ denotes effective time

$$\xi(t) = \int_0^t \frac{dt'}{\tau} \tag{12}$$

It can be shown that Eq.(11) reduces to the quasi-static result when the product of relaxation time and the rate of change approaches zero. In the quasi-static model, non-isothermal crystallization rate reduces to a unique function of temperature (stress) and does not depend on cooling rate (stress rate). The actual steady-state function K_{st} (T, Δp) can be found from crystallization experiments made under different, but constant conditions. No additional material characteristics are needed.

Non-isothermal crystallization experiments performed at constant cooling rates demonstrate that the quasi-static model does not hold true: crystallization rate depends not only on temperature, but also on cooling rate. An example for poly(ethylene terephthalate) is shown in Figure 2 [15].

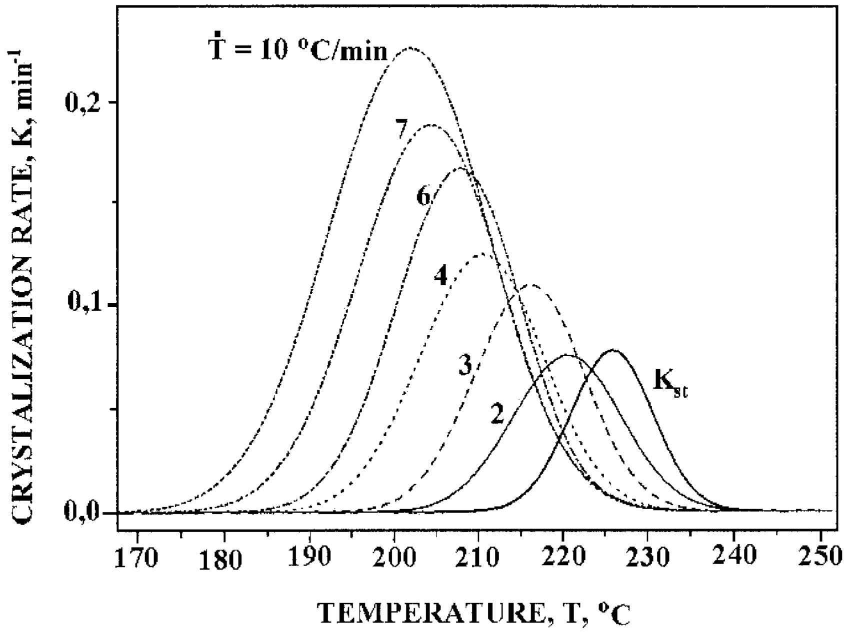

Figure 2. Non-isothermal crystallization rates, K, for poly(ethylene terephthalate) as functions of temperature [15]. Cooling rates indicated.

With increasing cooling rate, maxima of the K(T) plots increase and move to lower temperatures. Similar results were obtained for isotactic polypropylene [16], poly(vinylidene difluoride) [17] and other polymers. Evaluation of the extended model (Eq.11) requires the knowledge of two additional characteristics: relaxation time, τ, and athermal nucleation function, f.

5. Stress- and orientation-dependent crystallization

Deformation of polymer chains leads to reduction of the configurational entropy of crystallization and, consequently, to elevation of melting temperature and increase in nucleation and crystallization rates. Average crystallization characteristics can be related to stress in the crystallizing polymer. This fact has been observed and described half a century ago in crosslinked rubbers [18-20]. Another effect is related to ***molecular orientation***. Oriented polymers (e.g. polymer melts subjected to elaongat-ional flow, or crosslinked rubbers in the deformed state) crystallize in a selective way: chain segments with orientations prevailing in the system (in uniaxially extended samples – segments oriented along the elongation axis) crystallize at higher temperat-ures and with higher rates than segments with infrequent orientations. This leads to preferential formation of highly oriented crystals and discrimination of crystals with other orientations.

In spite of theoretical predictions [8] and some experimental observations [21,22], very few quantitative data on stress-affected crystallization rates are available, and much more so on the effects of molecular orientation. Some model relations between average molecular orientation (or stress) have been described in the book on fiber spinning [23]. Experiments made by Smith & Steward [24] and Alfonso, Verdona & Wasiak [25] on preoriented polyethylene terephthalate, show increase in crystallizat-ion rates by several orders of magnitude. To describe effects of average molecular orientation, f_{or}, Ziabicki proposed a semi-empirical equation [26], which for not too high degrees of orientation reduces to the form

$$K_{st}(T, f_{or}) \cong K_0(T)\ exp[Af_{or}^2] \qquad (13)$$

including a single orientation sensitive function, A. Assuming proportionality between orientation factor and tensile stress, local degree of molecular orientation can be re-placed by local values of the normal stress difference, $\Delta p = T_{33} - T_{11}$. For modelling purposes, temperature-dependent part of the steady-state crystallization rate can be represented by the empirical formula [9]

$$\begin{aligned} &K_0(T) = K_{max}\ exp\left[-4\,ln\,2\frac{(T - T_{max})^2}{D_{1/2}^2}\right] && \text{for } T_g < T < T_m \\ &K_0(T) = 0 && \text{for } T \le T_g \text{ or } T \ge T_m \end{aligned} \qquad (14)$$

Crystallization disappears above melting temperature, T_m, and below glass transition temperature, T_g. Determination of temperature- and stress-controlled crystallization characteristics provides a challenge for experimental polymer physics. Reliable and reproducible information about crystallization rates is a necessary condition of effective modeling.

6. Effect of crystallization on rheological properties of the polymer

In industrial processes, a viscous or viscoelastic fluid is converted into a plastic or elastoplastic solid. Using the simplest constitutive equation, one for an incompressible Newtonian fluid

$$\mathbf{T} = 2\eta\mathbf{D} = \eta\left[\nabla\mathbf{v} + (\nabla\mathbf{v})^{T}\right] \tag{15}$$

where **D** is deformation rate tensor, one can describe solidification by variation of the viscosity function, η. Viscosity strongly decreases with increasing temperature. It is only natural to assume that crystallization, resulting in formation of intermolecular bonds („physical crosslinks"), after reaching some critical level, will reduce irreversible deformation to zero, i.e. raise the apparent viscosity to infinity. In a paper concerned with mechanics of melt spinning [27] we have used an empirical relation for temperature- and crystallinity-dependent viscosity

$$\begin{aligned} &\eta(T,x) = \eta_0(T)\cdot\left(\frac{1}{x - x_{cr}}\right)^{a} && \text{for } x < x_{cr} \\ &\eta(T,x) = \infty && \text{for } x \geq x_{cr} \end{aligned} \tag{16}$$

Before reaching critical crystallinity level, x_{cr} (estimated as 10%, or less), viscosity changes continuously with temperature and crystallinity. A convenient form of the $\eta_0(T)$ function is provided by WLF or Arrhenius models.

7. Example: crystallization in fiber spinning

Polymer melt with initial temperature T_0 is extruded through the spinneret with average linear velocity v_0, into the three-zone conditioning atmosphere. The first and the third zones are designed to quench the melt; the second zone is provided by a heating tube with controlled temperature. At the end of the third zone, the filament is wound with take-up velocity, v_L. T_0, v_0, and v_L provide boundary conditions for the process. We have analyzed melt spinning of poly(ethylene terephthalate) fibers. PET is a slowly crystallizing polymer: in the absence of stress, temperature-controlled crystallization rate is insufficient to produce significant amount of crystallinity within the period spent by the material in the crystallization interval (T_m,T_g). Slow spinning of PET ($v < 3{,}500$ m/min) yields glassy, amorphous fibers. At higher speeds, however (v_L = 3,500 – 10,000 m/min), stress-induced crystallization yields crystalline fibers with very high degree of crystal orientation (f_{cr} = 0.9-0.98). At the same time, molecular orientation factor, f_{am}, does not exceed 0.42 (Figure 3).

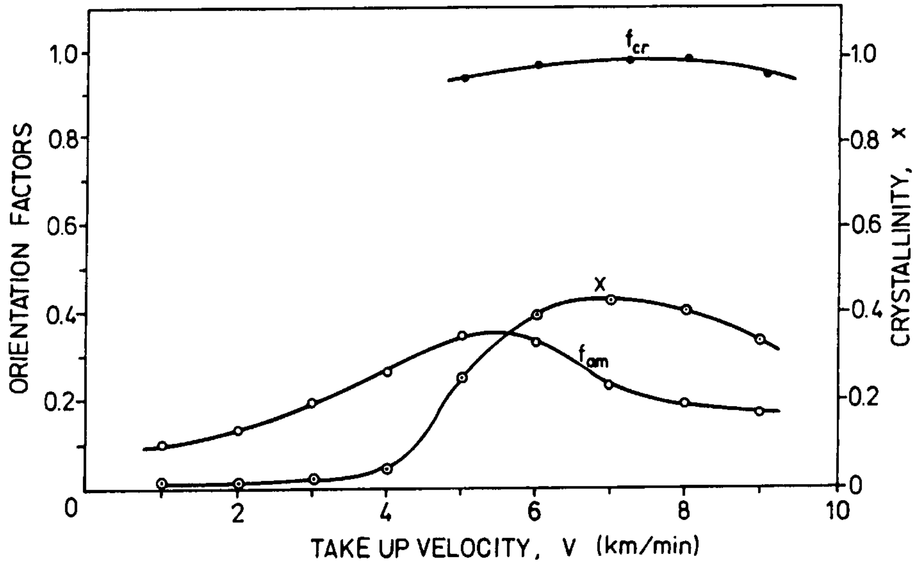

Figure 3. Crystallinity, x, crystal- and amorphous orientation factors (f_{cr}, f_{am}), for poly(ethylene terephthalate) fibers melt-spun at different speeds, v [21].

High degrees of crystal orientation at moderate orientation of crystallizing segments provide evidence for ***selective crystallization***. In a set of differently oriented chain segments, the first segments which crystallize, are those oriented along the main orientation (tensile stress) axis.

We have analyzed dynamics of melt spinning, incorporating quasi-static, temperature-, and stress-controlled crystallization rates from Eqs. (13), (14), and crystallinity-dependent viscosity from Eq.(16). Figures 4-6 present local velocity, stress and temperature profiles [28] for a selected set of spinning conditions with two values of the stress-sensitive crystallization rate factor. A = 0 results in negligible crystal-lization, A = 510 - in strong stress-induced crystallization. In the crystallizing filament velocity (Figure 4) and tensile stress (Figure 5) increase more rapidly than in an amorphous filament.

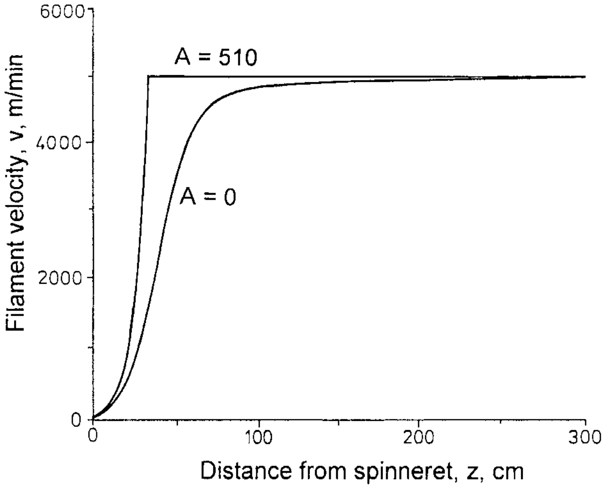

Figure 4. Local velocity for a poly(ethylene terephthalate) filament, as a function of the distance from spinneret [28]. Take-up speed, v_L = 5,000 m/min, filament thckness - 5 den. Stress-sensitive crystallization factor A, indicated.

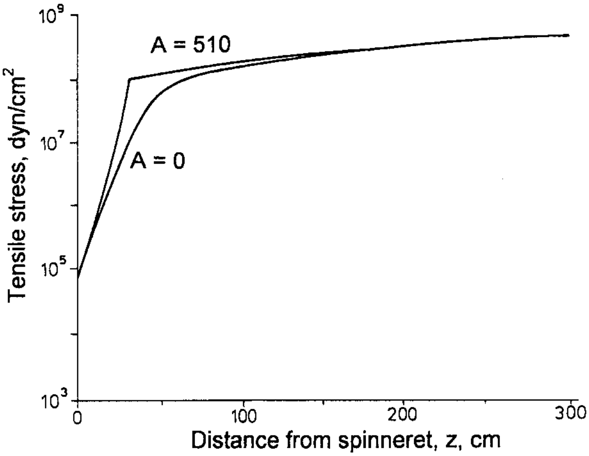

Figure 5. Local tensile stress for poly(ethylene terephthalate) filament, as a function of the distance from spinneret [28]. Take-up speed, v_L = 5,000 m/min, filament thickness - 5 den. Stress-sensitive crystallization factor A, indicated.

Filament temperature, monotonically dropping in the first quenching zone in a non-crystallizing filament (A = 0), shows an exothermal peak when crystallization is induced by stress (Figure 6).

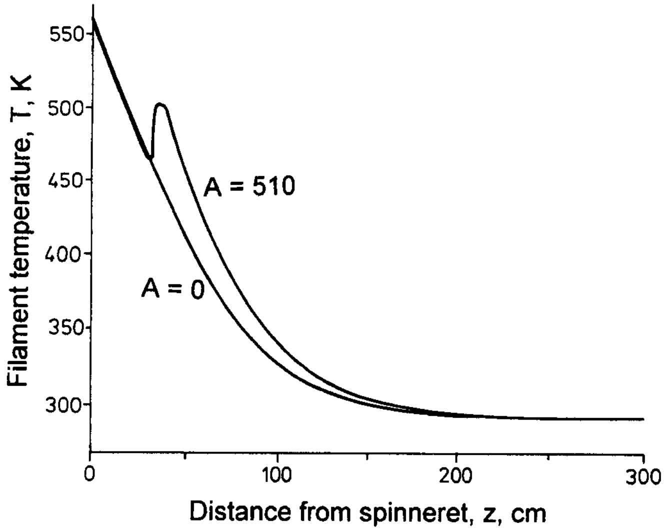

Figure 6. Local temperature for a poly(ethylene terephthalate) filament, as a function of the distance from spinneret [28]. Take-up speed, v_L = 5,000 m/min, filament thckness - 5 den. Stress-sensitive crystallization factor A, indicated.

More thorough analysis of the dynamic equations [29] shows that crystallization brings about bifurcation of the solutions. For A = 0 initial tension in the spinline, F_0, is a unique function of the assumed take-up velocity v_L. At higher A, however, the same speed can be realized by two or three different tensions [29]. The solutions differ in the conditions in which the polymer crystallizes and in the degree of crystallinity produced. Rapid crystallization leading to solidification of the polymer, may eventually exclude deformation of the spinline. Consequently, the maximum take-up speed (associated with rapid solidification) is limited (Figure 7). This limitation is less severe when „hot tube" is applied.

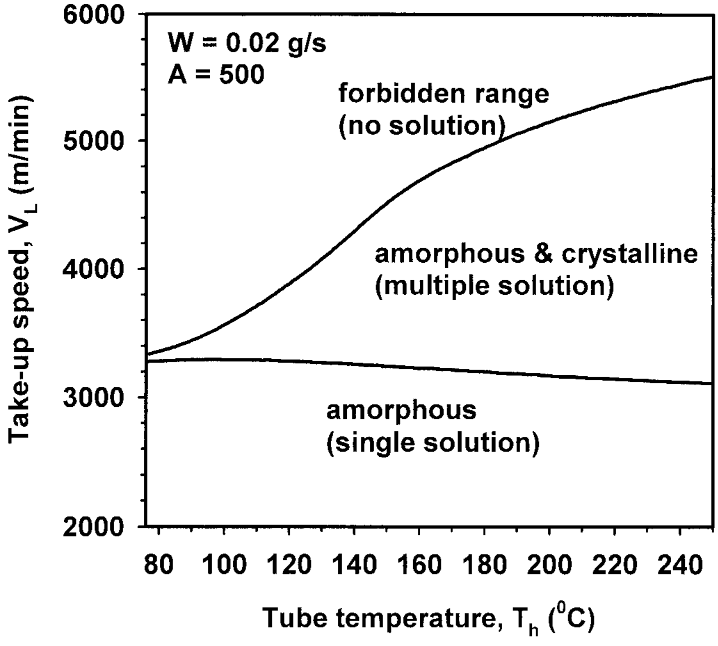

Figure 7. Characteristic regions in the space of spinning conditions for poly(ethylene terephthalate) crystallizing under stress [29]. Stress-sensitive crystallization factor A = 500, extrusion rate per filament, W = 0.02 g/sec.

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