



Feature article:

The role of flow-induced crystallisation in melt spinning

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Abstract: Flow-induced crystallisation in the course of melt spinning changes properties of as-spun fibres and modifies dynamics of the process. Velocity, stress and temperature profiles depend on the speed of on-line crystallisation. Very important but little studied is coupling between crystallinity and rheological properties of the polymer melt. Effects of crystallisation on the dynamics of melt spinning and on the rheological behaviour have been discussed and compared with model calculations and available experimental data.

Introduction

Dynamics of industrial processes are described by a set of governing equations including conservation of mass, momentum and energy, constitutive equations, describing properties of the material, and appropriate boundary conditions. Constitutive equations include rheological relations between stress and deformation, as well as other physical characteristics. In polymers, material properties strongly depend on molecular and supramolecular structure.

Flow affects structure development and itself is affected by structure. Therefore, the set of governing equations for melt spinning includes also structure evolution equations. Important structural characteristics include degree of crystallinity, size, shape and orientation of crystals, morphology of crystals, and molecular orientation of the uncrystallised polymer. Crystallisation contributes to energy balance and temperature distribution, directly and indirectly affecting rheological properties of the spinning line. The governing equations of melt spinning are mutually coupled.

The conditions in melt spinning dramatically differ from those encountered in laboratory experiments. In contrast to usual laboratory studies, temperature of a melt-spun

polymer locally changes in time with rates reaching $10^3 - 10^4$ K/s. In thicker filaments, radial temperature gradients may affect the resulting structure and properties.

In multifilament spinning, different temperatures and cooling rates are experienced by individual filaments. Tensile stress in the spin-line varies significantly along the filament axis. All this requires that crystallisation kinetics should be described as a process with rapidly changing, non-uniform conditions.

Crystallisation kinetics

The model of evolution of crystallinity starts with a statistical-geometrical formalism developed by Kolmogoroff [1], Avrami [2], Johnson & Mehl [3] and Evans [4]. Spontaneous formation of crystal nuclei and their subsequent growth in $m - 1$ dimensions results in a time-dependent degree of transformation (degree of crystallinity), X

$$X(t) = 1 - \exp[-E(t)] \quad (1)$$

where

$$E(t) = \text{const.} \int_0^t \dot{N}(s) ds \left[\int_s^t G(z) dz \right]^{m-1}; E \in (0, \infty) \quad (2)$$

is the expectancy of covering the space by 'phantom crystals'. \dot{N} and G represent nucleation and linear growth rates.

Non-isothermal crystallisation

Eqs. (1) and (2) can be used for the description of any transformation process, isothermal or non-isothermal, provided that the appropriate time functions $\dot{N}(t)$ and $G(t)$ are known. Nucleation and growth rates are described by thermodynamic models taking into account molecular characteristics of crystalline aggregates and their mode of growth.

Separate experimental determination of nucleation and growth rates is rather difficult, and in the description of non-isothermal crystallisation two different material functions, \dot{N} and G , are often replaced by a single, global crystallisation rate function, K

$$E(t) = \ln \left[\frac{1}{1 - X(t)} \right] \cong \left[\int_0^t K(t') dt' \right]^m \quad (3)$$

$K(t)$ is not a material characteristic because it may depend on the dynamics of the process, as well as on material properties. The Avrami exponent, m , has to be evaluated from other sources of information.

The early models of non-isothermal crystallisation [5-8] considered a quasi-static process, in which crystallisation rate followed in time changing external conditions, but did not depend explicitly on time or rates of change of thermodynamic variables. Some authors [8] assumed that functions $\dot{N}(t)$ and $G(t)$ were proportional to each other (isokinetic assumption), which yielded a result equivalent to Eq. (3). A more general model of non-isothermal crystallisation has been proposed by Ziabicki [9-12]. Two new effects absent in isothermal, or quasi-static models have been introduced: athermal nucleation and relaxation.

Stress- and flow-induced crystallisation. Average behaviour

Deformation of polymer chains leads to reduction of the configurational entropy, elevation of melting temperature, and increase of nucleation and crystallisation rates. The average crystallisation characteristics can also be affected by stress. This fact has been recognised long ago in stretched rubbers.

Stress (molecular orientation) introduces more than small correction to crystallisation. Melting (crystallisation) temperatures are elevated by tens of degrees and crystallisation rates increase by orders of magnitude compared to quiescent, stress-free conditions. Early literature on stress-induced crystallisation has been reviewed [13].

In spite of reasonably good understanding of the phenomenon, quantitative information on flow-induced crystallisation rates is scarce. Nevertheless, corrected thermodynamic calculations yield nucleation rate increase of the order $10^5 - 10^{15}$ and experiments of Smith & Steward [14] and Alfonso, Verdone & Wasiak [15] on pre-oriented poly(ethylene terephthalate) (PET) indicate $10^3 - 10^5$ fold increase in global crystallisation rates.

To describe effects of average molecular orientation, we have proposed a semi-empirical equation [13,16,17], which for not too high degrees of orientation reduces to the square term including a single orientation-sensitive function, A

$$K_{st}(T, f_{am}) = K_0(T) \exp(Af_{am}^2 + Bf_{am}^3 + \dots) \cong K_0(T) \exp(Af_{am}^2) \quad (4)$$

Assuming proportionality between average molecular orientation and stress, the amorphous orientation factor, f_{am} , can be replaced by the normal stress difference (tensile stress), $\Delta p = p_{33} - p_{11}$

$$K_{st}(T, \Delta p) \cong K_0(T) \exp[A'(\Delta p)^2] \quad (5)$$

For modelling purposes, the temperature-dependent part of the steady-state crystallisation rate can be represented by another empirical formula [5,6,13]:

$$K_0(T) = K_{max} \exp\left[-4 \ln 2 \frac{(T - T_{max})^2}{D_{1/2}^2}\right] \text{ for } T_g < T < T_m \quad (6)$$
$$K_0(T) = 0 \text{ for } T \leq T_g \text{ or } T \geq T_m$$

Selective crystallisation

Orientation of chain segments within a deformed chain leads to another important effect. Segments with orientations prevailing in the system (in melt-spinning: segments parallel to the filament axis) crystallise at higher temperatures and with higher rates than segments with less frequent orientations. This leads to preferential formation of axially oriented crystals, and discrimination of crystals with orientations perpendicular to the main axis [18-21]. Experimental evidence about selective crystallisation is scarce and indirect. The observation that supports this concept is comparison of crystal and amorphous orientation factors in a system crystallised under stress or flow.

Fig. 1 presents orientation factors for high-speed-spun PET fibres as functions of spinning speed [22,23]. It is evident that crystal orientation is nearly perfect ($f_{cr} = 0.9 - 0.98$), while average orientation of the untransformed amorphous segments does not exceed the value of $f_{am} = 0.42$. High degrees of crystal orientation and moderate orientation of crystallising segments provide an indirect evidence of selective crystal-

lisation. Also other experimental observations support the concept of orientation-differentiated behaviour of polymer crystallisation in a flow field [24-26].

Experimental determination of crystallisation kinetics in a wide range of conditions (temperature, stress, cooling rates, etc.) is a challenge for polymer physics and polymer engineering. Accumulation of reliable quantitative information about crystallisation is one of the necessary prerequisites of effective modelling.

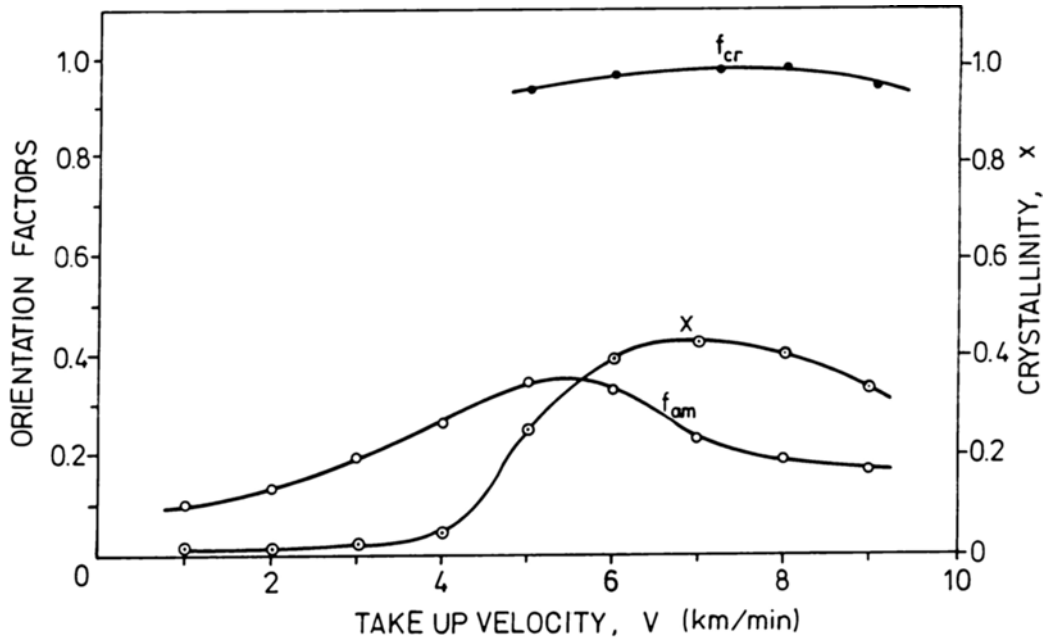


Fig. 1. Crystallinity, X , and orientation factors, f_{cr} , f_{am} , for PET fibres melt-spun at different take-up speeds, V_L [23]

Simulation of melt spinning from a crystallising polymer

To explain the consequences of polymer crystallisation for the dynamics of melt spinning, we have analysed steady-state melt spinning of PET fibres into a three-zone conditioning atmosphere [27,28]. The first and the third zone were designed to quench the melt; the second one is a heating tube with controlled temperature. At the end of the third zone, the filament is wound with constant velocity, V_L .

Extrusion temperature T_0 , average extrusion velocity V_0 , and take-up velocity V_L provide boundary conditions. PET is a slowly crystallising polymer: in the absence of stress, crystallisation is very slow. Spinning with small take-up velocities ($V_L < 3500$ m/min) yields glassy, amorphous fibres. At higher speeds ($V_L = 3500 - 10\,000$ m/min), flow-induced crystallisation yields crystalline fibres with very high degree of crystal orientation (Fig.1).

In our simulations, temperature- and orientation-dependent crystallisation rates from Eqs. (4) and (5) were used together with position-dependent polymer viscosity

$$\eta(z) = \eta[T(z), X(z)] \quad (7)$$

where z is the axial distance from the spinneret, and the viscosity function is taken from ref. [29] (cf. Eq. (11) below).

Local viscosity was assumed to grow to infinity when crystals, acting as 'physical crosslinks' led to complete solidification of the melt. Figs. 2 - 4 present velocity, stress

and temperature profiles for a selected set of spinning conditions with two values of the orientation-sensitive crystallisation rate factor.

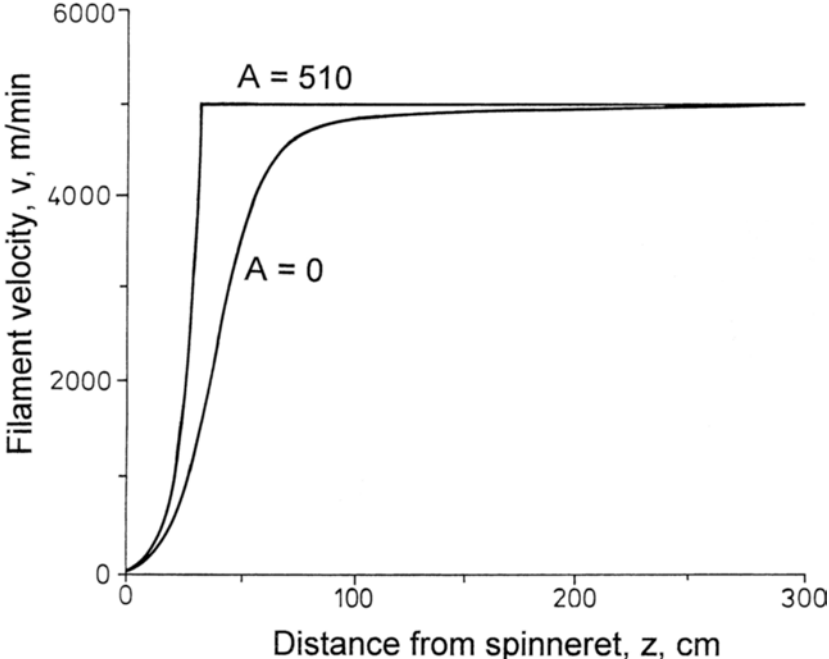


Fig. 2. Local velocity for a PET filament, as a function of the distance from spinneret, z [27]. Take-up speed $V_L = 5000$ m/min, filament thickness 5 den. Orientation-sensitive crystallisation factor A indicated

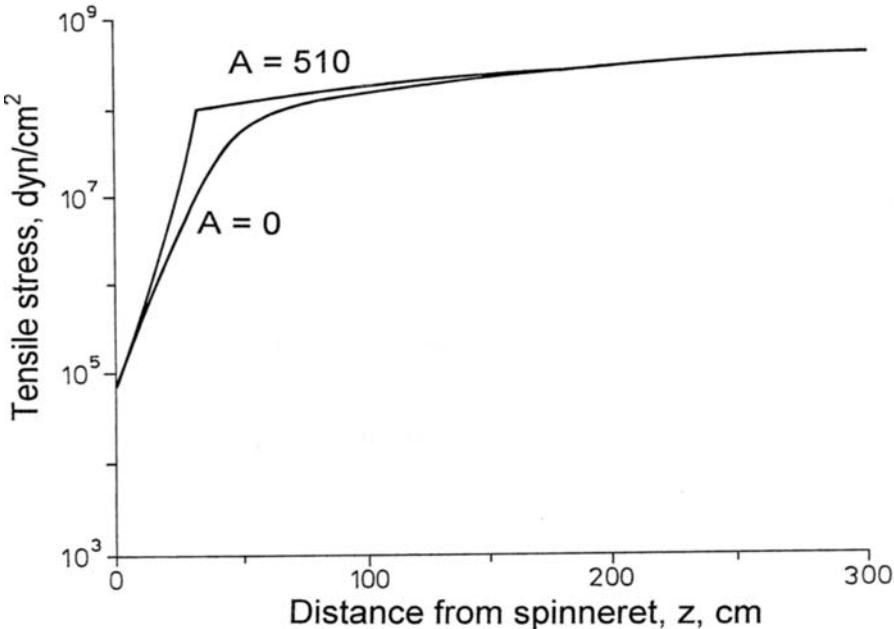


Fig. 3. Local tensile stress for a PET filament, as a function of the distance from the spinneret [27]. Take-up speed $V_L = 5000$ m/min, filament thickness 5 den. Orientation-sensitive crystallisation factor A indicated

$A = 0$ results in negligible crystallisation, $A = 510$, based on rough experimental estimates [14,15], corresponds to crystallisation strongly enhanced by flow (stress).

Both, filament velocity (Fig. 2) and tensile stress (Fig. 3) increase more steeply in the presence of flow-induced crystallisation.

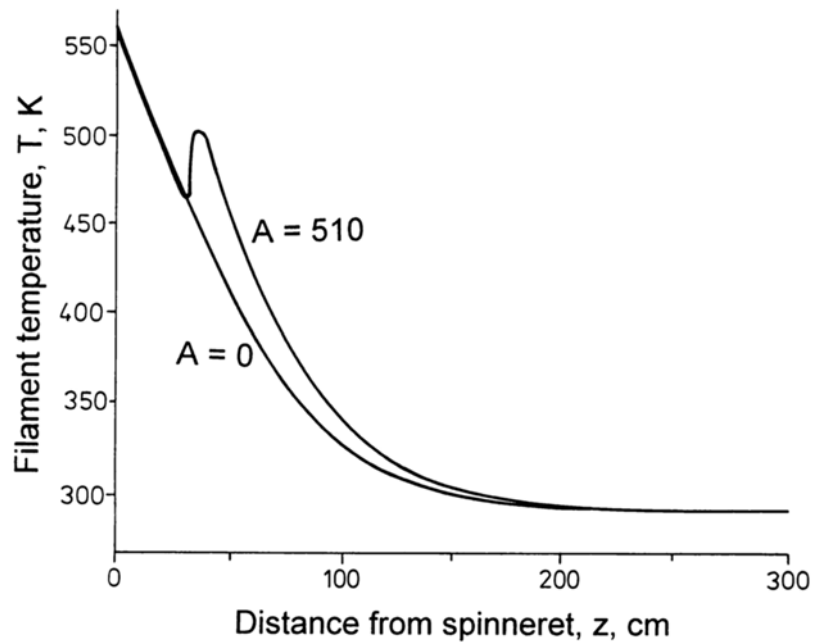


Fig. 4. Local temperature for a PET filament, as a function of the distance from the spinneret [27]. Take-up speed $V_L = 5000$ m/min, filament thickness 5 den. Orientation-sensitive crystallisation factor A indicated

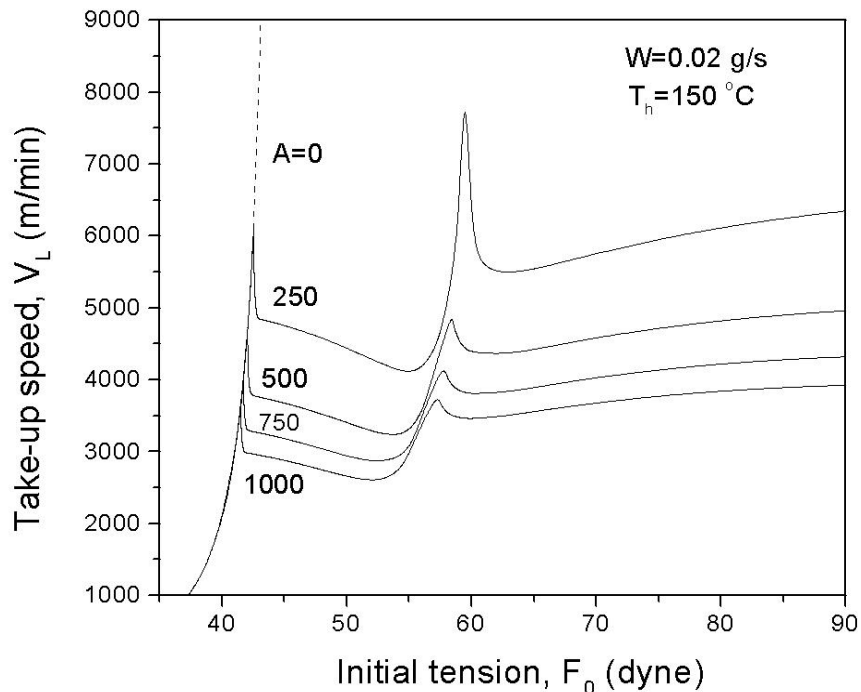


Fig. 5. Take-up speed, V_L , vs. initial tension, F_0 , for PET fibres for different values of the orientation-sensitive crystallisation factor A . Tube temperature, $T_h = 150^\circ\text{C}$ [28]

Filament temperature (Fig. 4) monotonically drops in a non-crystallising filament ($A = 0$), and shows an exothermal peak when crystallisation is induced by stress (orien-

tation), $A = 510$. More thorough analysis shows that crystallisation induces bifurcation of the solution of the governing equations (Fig. 5). For $A = 0$ the initial tension in the spin-line, F_0 , is a unique function of the assumed take-up velocity V_L . At higher A , however, the same speed can be realised by two or more different tensions [28]. The solutions differ in the conditions under which the polymer crystallises and in the degree of crystallinity produced.

Fig. 6 presents various areas in the space of spinning conditions ‘tube temperature \times take-up velocity’. Individual areas correspond to purely amorphous fibres, multiple solutions yielding amorphous or crystalline fibres, and a ‘forbidden range’ in which no steady-state spinning is possible. Rapid crystallisation leading to solidification of the polymer may eventually exclude deformation of the spin-line (‘forbidden range’). Limited take-up speed is less severe when a hot tube is applied (Fig. 6).

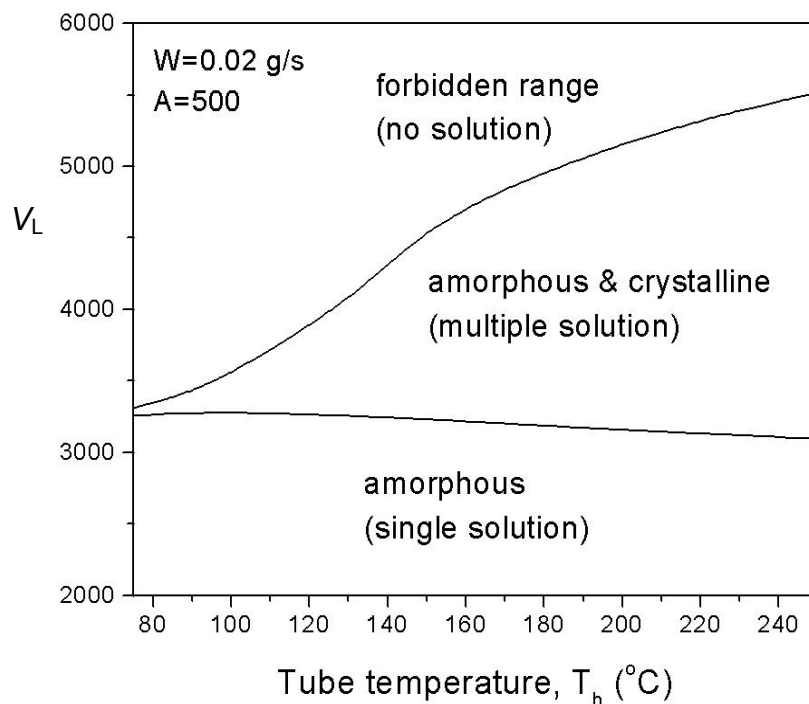


Fig. 6. Space of spinning conditions for PET crystallising under stress [28]. Stress-sensitive crystallisation factor, $A = 500$; extrusion rate per filament, $W = 0.02$ g/s

Strong effects of crystallisation predicted by our model are as true as the assumptions made in the simulation. The weakest point is the, rather arbitrarily assumed, relation between crystallinity and rheological behaviour of the melt.

Rheological properties of crystallising polymer melts

Under industrial conditions, a viscous or viscoelastic fluid is converted into a plastic or elastoplastic solid. Using the constitutive equation for an incompressible Newtonian fluid with variable viscosity, treating melt spinning as a purely elongational flow, one obtains the relation between tensile stress, Δp , and elongation rate, $\partial V_z / \partial z$

$$\Delta p = p_{33} - p_{11} = 2\eta(D_{33} - D_{11}) = 3\eta \frac{\partial V_z}{\partial z} \quad (8)$$

3η is often known as ‘elongational viscosity’. Solidification may be realised by variation of viscosity, η , controlled by local temperature, $T(z)$, and crystallinity, $X(z)$.

Models of crystallinity-controlled viscosity

The simplest model of a partly crystallised fluid is provided by the theory of suspensions. Solid particles (crystals) suspended in a viscous fluid contribute to the viscosity of the suspension

$$\frac{\eta}{\eta_0} = 1 + 2.5\varphi + 5.01\varphi^2 + \dots \quad (9)$$

where φ is the volume fraction of the suspended solid (= degree of crystallinity). An empirical relation for suspensions has been postulated by Krieger and Dougherty [30] in the form

$$\frac{\eta}{\eta_0} = \left[\frac{1}{1 - \varphi/\varphi_m} \right]^{2.5\varphi_m} \quad (10)$$

which reduces to the Einstein result at small concentrations and reaches infinity at the limit of critical concentration, $\varphi \rightarrow \varphi_m$. Experimental measurements on suspensions support the above formula and made it popular, also in the field of polymer processing [31,32].

On the other hand, it is hard to believe that a dilute suspension may provide a realistic model for a partly crystallised polymer melt composed of long polymer chains. An alternative concept [29] considers crystals as ‘physical crosslinks’ connecting polymer chains in the melt. Following this idea, we have proposed an empirical relation between temperature, crystallinity and viscosity in the form [29]:

$$\eta(T, X) = \eta_0(T) \cdot \left(\frac{1}{1 - X/X_{cr}} \right)^a \quad \text{for } X < X_{cr} \quad (11)$$

$$\eta(T, X) = \infty \quad \text{for } X \geq X_{cr}$$

The ideal steady-state rheological behaviour of a crosslinking system is shown in Fig. 7. The increase of viscosity in the range $X < X_{cr}$ is caused by aggregation of polymer chains. In the vicinity of X_{cr} (equivalent to the gel point in chemical crosslinking), the fluid melt is converted into an elastic solid, the viscosity asymptotically approaches infinity and the material becomes incapable of flowing.

A rough estimate of X_{cr} is based on the classical theory of crosslinking. Consider a polymer melt composed of n_{ch} chains with primary (uncrosslinked) degree of polymerisation N_0 . The molecular volume of a single unit (mer) is v_0 . Crystallisation to volume fraction X introduces n_x crystalline crosslinks, each with volume v_x . Neglecting volume changes on crystallisation, we have

$$X = \frac{n_x \cdot v_x}{n_{ch} \cdot N_0 \cdot v_0} \quad (12)$$

The first fraction in Eq. (12) characterises the crosslink density, i.e., the number of crosslinks (crystallites, nuclei) per primary chain. The second one is the ratio of crystal (crosslink) volume to that of a single macromolecular chain. The critical crystallinity for crosslinking (gelation condition) corresponds roughly to two crosslinks per primary chain, yielding

$$X_{cr} = 2 \frac{v_x}{N_0 \cdot v_0} \quad (13)$$

It is evident that X_{cr} is inversely proportional to the degree of polymerisation N_0 (molecular weight) of the polymer. The number of mer units contained in an effective crosslink should not exceed 5 - 50. The degree of polymerisation, N_0 , for typical fibre-forming polymers ranges from 200 (PET) to 4000 (polypropylene). Consequently, critical crystallinity may be as small as a few percent. Without knowing actual values, in our simulation [29,30] we have assumed $X_{cr} = 0.1$ and $a = 1$.

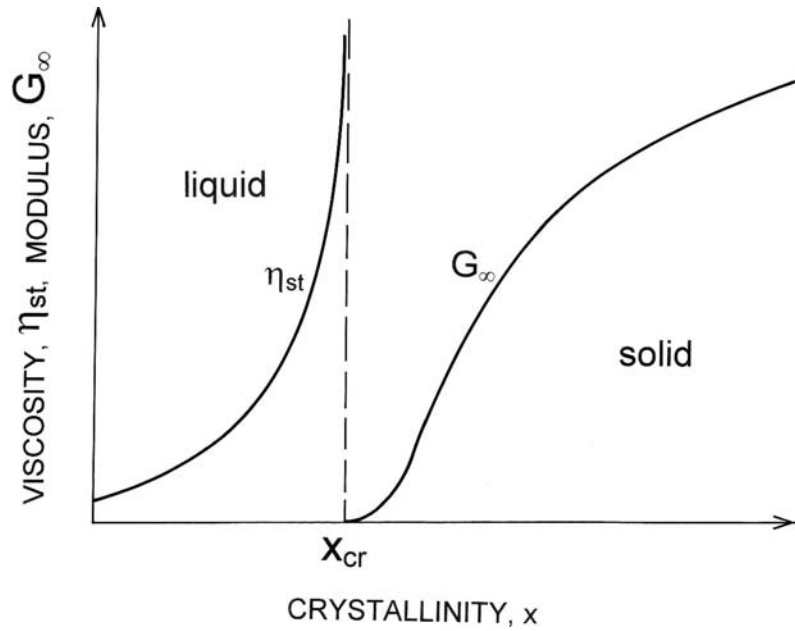


Fig. 7. Expected variation of steady-state viscosity, η_{st} , and steady shear modulus, G_{∞} , in a crystallising (crosslinking) polymer melt as a function of crystallinity, X (crosslink density)

Surprisingly, our Eq. (11), based on the crosslinking concept, reduces to the Krieger-Dougherty relation Eq. (10), when crystallinity X is identified with the volume fraction of the suspended solid, ϕ , and $a = 2.5 \phi_m$. The similarity has purely formal character. The critical volume fraction ϕ_m in the experiments used by Krieger & Dougherty for verification of their model amounted to 54% and 67% while the theory of crosslinking and experimental data (see section 5.2. below) point to X_{cr} in the range of 1% - 10%.

Several authors analysing melt processing of crystallisable polymers proposed empirical relations between viscosity and crystallinity. Katayama and Yoon [33] assumed a linear function

$$\frac{\eta}{\eta_0} = 1 + 99X \quad (14)$$

while Shimizu, Okui and Kikutani [34] suggested an exponential relation

$$\frac{\eta}{\eta_0} = \exp(cX^d) \quad (15)$$

and the group of Titomanlio [35,36] assumed

$$\frac{\eta}{\eta_0} = 1 + f_1 \exp(-f_2 / X^m) \quad (16)$$

Fig. 8 presents viscosity-crystallinity functions calculated by Sorrentino [37] from different models. Whereas our model predicts a vertical asymptote at small X , other relations yield finite viscosity up to $X = 1$.

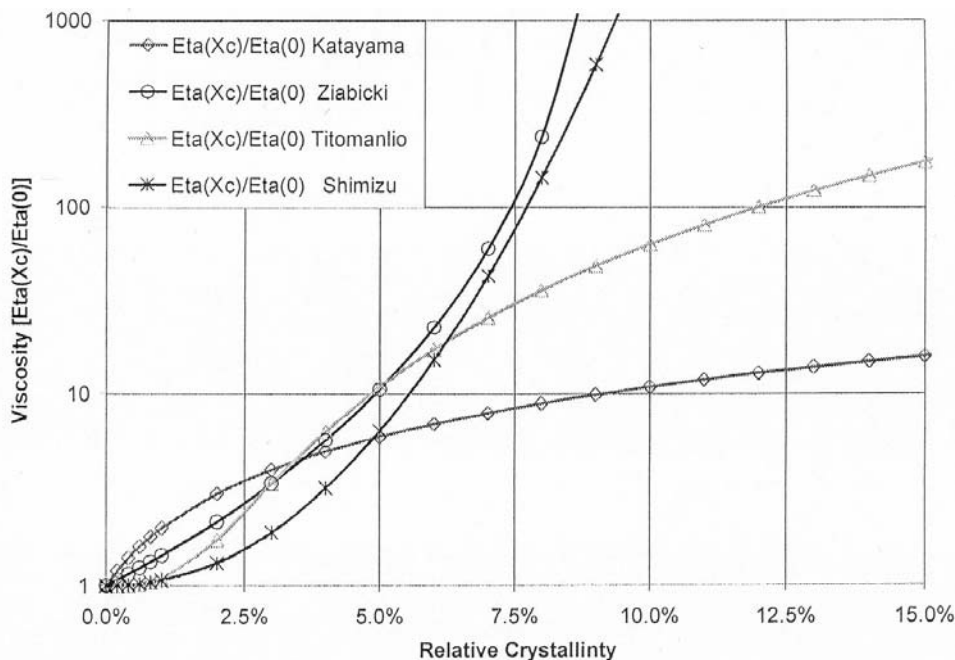


Fig. 8. Viscosity-crystallinity relations calculated from different models [37]

Experimental evidence

Different predictions about the behaviour of melt viscosity on crystallisation lead to the fundamental question: does a small amount of crystallinity cause complete solidification (i.e., infinite viscosity) of the melt? Early observations of Kobayashi and Nagasawa [38,39] seem to support the solidification concept. The authors observed the behaviour of a polyethylene melt in a rotating viscometer. As a result of crystallisation the melt was converted into a solid.

More recently, experimental data on the viscosity of crystallising polymer fluids have been reported. Pantani, Speranza and Titomanlio [36] measured the complex viscosity and, in a parallel experiment, development of crystallinity in a polypropylene melt. A similar approach has been applied by the group of Winter [40] to thermo-elastic polypropylene (TEPP). The original results converted by Sorrentino to the 'viscosity-crystallinity' scale (Fig. 9) indicate a slow increase of complex viscosity in the entire range of crystallinity, also in the region defined as 'gelation'. The gelation point, identified in ref. [40] at a few percent crystallinity, is not accompanied by any dramatic change of complex viscosity.

In contrast to dynamic measurements, steady shear experiments show a rapid upturn of steady state viscosity in the time of flow (crystallisation) [35,41,42]. Conversion of the Floudas results [46] to crystallinity scale (Fig. 10) indicates a critical crystallinity X_{cr} in the range of 0.03 - 0.15 dependent on the shear stress applied. This is consistent with the crosslinking mechanism. The position of the upturn point (critical

crystallinity) is not a constant. In the range of small shear stresses, X_{cr} moves with increasing stress to smaller crystallinity. At higher stresses the reverse is true, which may suggest destruction of crystals (crosslinks) by flow. A similar upturn of steady-state viscosity vs. time was observed by Titomanlio, Speranza and Brucato [35], and Wassner & Maier [42].

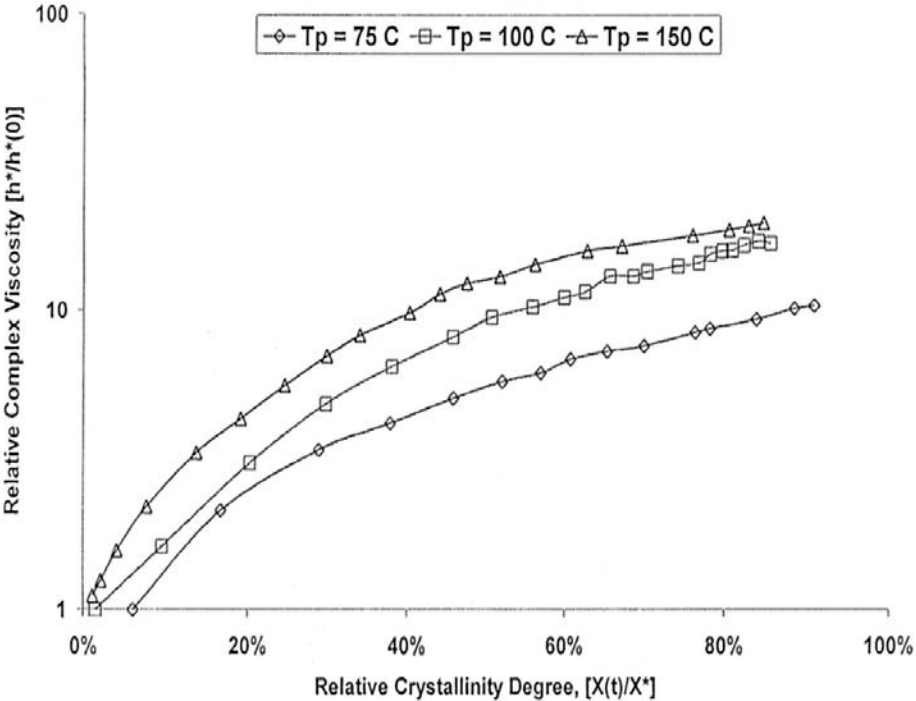


Fig. 9. Reduced complex viscosity vs. crystallinity for thermoelastic polypropylene. Data from Lin et al. [40], converted by Sorrentino [37]

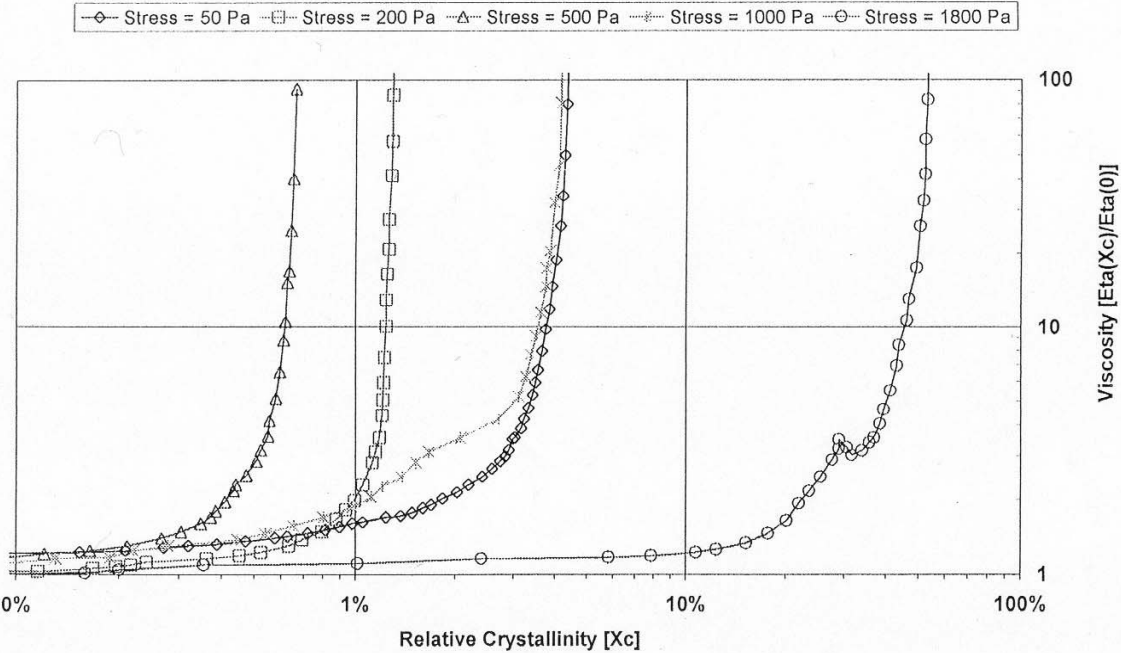


Fig. 10. Reduced steady-state viscosity vs. crystallinity for polypropylene melt. Data from Floudas et al. [40], converted by Sorrentino [37]

Significance of the rheological behaviour of crystallising polymers for polymer processing has recently been recognised by many research groups. On-line measurements, characterising local dynamics and structure development, are in the centre of interest. Rheo-optical behaviour [43-46] and a combination of rheology with high-intensity X-ray diffraction [47-50] are being studied. In the US, government sponsored studies are carried out by consortia coordinated by the National Institute of Science and Technology [51,52].

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