

REPORT

Crystallization Kinetics in Polymer Melts

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ABSTRACT

Differences in the levels of crystallinity within injection moulded items can cause warpage due to differential shrinkage. These variations can reflect uneven cooling of the item or differences in the alignment of the polymer chains during processing. A number of models have been proposed to describe the crystallization of polymers as a function of temperature, pressure and shear stress, i.e. the conditions experienced during injection moulding. This review describes some of these models and their limitations.

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1. INTRODUCTION

The injection moulding industry is experiencing ever increasing commercial pressures to manufacture articles at lower cost. Costs can be reduced by, for example, shortening the lead times between design and production, optimising processing conditions to reduce cycle times and by improving designs to use materials more efficiently ¹. Solutions to these problems have been greatly assisted by the comparatively recent development of commercial software packages such as Moldflow ², C-Mold ³ and Fillcalc ⁴ that simulate the injection moulding process. Such software can be used as tools to explore the influence of different design strategies, materials and processing conditions on the quality of the resultant 'product' ^{1,5}. These predictions have been compared with the behaviour of 'real' mouldings in a number of validation exercises ⁶⁻¹⁰.

Some of the packages have the capacity to calculate the dimensional stability of moulded articles ^{2,3}. This is a particularly important aspect of design, particularly for parts manufactured from semicrystalline polymers where shrinkage and warpage behaviour is an important consideration. However the warpage analysis modules currently available in injection moulding simulation software packages tend to predict trends in dimensional instability of moulded parts rather than absolute values. This can give rise to a disparity between predicted and observed behaviour. This mismatch reflects errors in estimating the level of distribution of crystallinity throughout the moulding and in calculating residual stresses.

The calculations used to predict dimensional instability require an understanding of how the crystallization behaviour of different polymers depends both on the thermomechanical history of the melt and its composition. Current versions of the software packages are limited in that the models they contain are only able to describe the crystallization behaviour of melts under isothermal conditions. More advanced models that are able to cater for the effects of nucleating agents or shear stresses on crystallization or describe crystallization under non-isothermal conditions are either unavailable or they have not yet been incorporated into the codes. One of the reasons for this omission is that in some cases there is no consensus of opinion as to which of the available models are most appropriate.

A number of recent reviews and symposia have summarized the current state of knowledge in the field of the crystallization kinetics of polymer melts and theories of crystal growth ¹¹⁻¹⁷. Much of the published literature on the subject of crystallization kinetics is concerned with the crystallization behaviour of melts under isothermal conditions. However such conditions rarely occur in manufacturing processes i.e. injection moulding. The rate at which material is cooled in a mould cavity can vary significantly throughout the moulding due to variations in thickness and with position with respect to the gate (or gates) and cooling lines. This situation is further complicated by the challenge of modelling the dynamics

of melt cooling to account for the latent heat of fusion evolved during crystallization that Friedl and McCaffrey¹⁸ have shown extends the cooling cycle.

This review provides a summary of functions that have been published in the literature that describe the kinetics of crystallization in polymer melts under iso- and non-isothermal conditions, including the effects of nucleating agents and shear-induced crystallization. Brief summaries of the techniques employed to monitor crystallization kinetics and a description of spherulite types are to be found in Appendices 1 and 2 respectively.

2. BACKGROUND

2.1 FACTORS AFFECTING CRYSTAL MORPHOLOGY

Certain mechanical and optical properties of semicrystalline polymers depend not only on the percentage of crystalline material present but also on the size of the crystals, their shape and their distribution. This is very apparent in, for example, parts thermoformed from high performance thermoplastic composites. In this process the matrix materials e.g. poly(ether ether ketone) (PEEK) are cooled at rates that can exceed a hundred degrees celcius per minute after being moulded over a heated former. This process can lead to the formation of amorphous regions within the material that have poor thermal and environmental resistance and inferior mechanical properties¹⁹⁻²⁴ in comparison with those of the semicrystalline areas.

The crystallization of molecules oriented by flow can improve material properties such as the strength of melt spun fibres or the clarity of films. The morphology of the spherulites formed in these melts reflects the amount of strain within the melt induced by flow (1-3). Spherulites formed under zero flow rate conditions i.e. zero strain are shown schematically in Figure 1a. Subjecting a melt to a low flow rate will cause the spherulites to distort as shown in Figure 1b with the chain-folded lamellae orienting themselves with respect to the flow direction. At high flow rates i.e. high strains the morphology changes from that of a distorted spherulite to a microfibrillar structure (Figure 1e) where the molecules are stretched in the flow direction. This molecular distortion is due to the elastic extension of the chain segments between molecular entanglements and occurs in both extensional flow^{25,26} and shear flow²⁷. In practice there is a complex interplay of flow rate with molecular orientation because of the competition between crystallization, slippage of molecular entanglements and stress relaxation of distorted molecules²⁸. Not surprisingly flow induced molecular orientation increases the overall level of crystallization and the rate at which the material crystallizes, with reports in the literature suggesting that it can be as much as 100 orders of magnitude faster than that which occurs in an isotropic medium^{12,29}. The final morphology of the crystals and level of crystallinity will also depend on the rate at which the melt is cooled and will

effectively cease when its temperature reaches the glass transition temperature, T_g . Crystal morphology is also affected by the molecular weight of the polymer, polydispersity, crystallization conditions and the stereochemistry of the chains. High molecular weight chains tend not to produce spherulites but random lamella structures whereas low molecular weight polymers have a tendency to crystallize in thin rod like structures or axialites. Thus spherulites are found only over a limited range of molecular weights and for certain crystallization conditions^{30,32}.

2.2 THE DRIVING FORCE FOR CRYSTALLIZATION

Crystal growth can be triggered by *homogenous* or *heterogenous nucleation*. In homogenous nucleation the natural density fluctuations that are present in the melt can become stable under certain conditions forming seed crystals. However, more often than not crystallization is triggered by the presence of heterogeneities i.e. impurities or specific additives that act as nucleation sites. Common additives such as pigments, reinforcing fibres or pigment carriers e.g. wax can act as nucleating agents, or specific materials known to induce crystallization such as sodium benzoate can be added to the feedstock. These nucleating agents can enhance crystallization rates by increasing the density of nuclei^{33,34} or by enhancing crystal growth through lowering the interfacial surface free energy^{35,36}. The efficiency of different types of nucleating agent depends on the polymer in question. Beck³⁷ and Binsbergen³⁸ have suggested criteria for ranking the effectiveness of different nucleating agents for isotactic polypropylene (iPP). This property can be usefully exploited to improve certain material properties, eg. the clarity of materials such as polypropylene³⁹ although for some materials or moulding conditions it can lead to excessive shrinkage or part distortion. The efficacy of nucleating agents seems to be independent of molecular weight. Beck⁴⁰ demonstrated that the acceleration of crystallization in the presence of the nucleating agent aluminium dibenzoate had very little dependence on molecular weight of specimens that varied by three orders of magnitude.

Crystallization of material from a melt is controlled by the Gibbs free energy, ΔG_f of the system. At the phase transition temperature at which crystallization occurs the free energies of both the melt (G_m) and solid state (G_c) are balanced such that $G_m = G_c$. The rate of crystallization at any other temperature is an exponential function of the energy difference $\Delta G_f = G_m - G_c$. Crystallization is promoted when ΔG_f is positive and melting when it is negative. This energy balance is critical for the development of homogenous nucleation sites resulting from the stabilization and enhancement of the natural concentration fluctuations that occur within melts.

It can be shown¹² that ΔG_f is approximately proportional to the degree of supercooling ΔT (where $\Delta T = T_m^0 - T$ and T_m^0 is the equilibrium melting temperature). ΔH_f is the heat of fusion released during the

melting of an infinitely large crystal and ΔS_f is the difference in entropy between molecules dispersed in a melt and those constrained within an ordered crystal. The equilibrium melting point T_m° can be higher in sheared melts due to the reduction in entropy that accompanies chain orientation. The amount that T_m° changes will reflect both the changes in entropy and enthalpy resulting from conformational rearrangements of the polymer chains. This increase in T_m° effectively explains why oriented melts crystallize so rapidly in comparison with unoriented melts over comparable temperature ranges.

3. MODELLING CRYSTALLIZATION KINETICS

3. INTRODUCTION

Plotting the degree of crystallinity against *logarithmic* time at a given temperature below the melting point shows a characteristic sigmoidal shape as shown in Figure 2⁴¹. A series of such plots obtained over a range of temperatures can be superimposed by horizontal shifts. This indicates that the temperature coefficient of the *rate* of crystallization is independent of temperature. The early stages of crystallization (*primary crystallization*) i.e. at times shorter than that corresponding to the inflection point of the sigmoidal curve - can occur very rapidly in materials such as polyethylene. Other polymers such as poly(ethylene terephthalate), (PET) crystallize at a much slower rate and hence have been the subject of many studies of crystallization kinetics. Beyond the inflection point crystallization occurs much more slowly (*secondary crystallization*) and this process can last for many decades of time in some polymers.

Modelling the kinetics of crystallization requires basic knowledge of how crystallization is affected by both temperature and molecular orientation. Often the only data available are obtained from studies of crystallization under quiescent isothermal conditions that are not applicable to manufacturing processes. In addition the isothermal data are typically confined to a narrow temperature band close to the melting point of the crystal T_m where the rate of crystallization is comparatively slow. Studies of this type are referred to as *melt crystallization*. At lower temperatures the rate at which the material crystallizes is generally too fast to be measured. However the rate slows down at temperatures approaching the glass transition temperature, T_g enabling additional kinetics data to be obtained. This data is obtained by rapidly cooling a melt to a temperature well below T_g to produce an amorphous sample. The sample is then heated to some temperature T slightly above T_g whereby crystallization then occurs. This process is referred to as *cold crystallization*. Non-isothermal measurements of crystallization can be made using either melt or cold crystallized specimens. However the cooling or heating rates that are practically accessible, up to $\sim 30^\circ\text{C}$ per minute, are significantly lower than those experienced in manufacturing processes such as injection moulding.

Equations that describe the kinetics of crystallization are typically of the form $dX_r / dt = J(T)f(X_r)$ where X_r is the fraction of crystallized material within the sample at a time t with respect to that which is found at very long times. The rate at which the material crystallises dX_r/dt is proportional to a temperature dependent rate constant $J(T)$ and some function of X_r . J typically has an Arrhenius dependence on temperature of the form $J = Z \exp(-E/RT)$ where Z is a pre-exponential coefficient and E is the activation energy for the process. In isothermal Differential Scanning Calorimetry (DSC) measurements the latent heat of crystallization evolved as a function of time represents dX_r/dt which can be determined at different temperatures.

3.2 ISOTHERMAL CRYSTALLIZATION

Many of the published functions for modelling isothermal crystallization are derived from that derived by Kolmogoroff⁴², Johnson and Mehl⁴³ and Avrami⁴⁴ which is of the form

$$X_r = 1 - \exp(-kt^n) \quad (1)$$

where X_r is the relative degree of crystallinity at some time t with respect to that which finally develops over a long period of time. In a DSC thermogram (Figure 3) the relative degree of crystallinity X_r is defined according to the ratio

$$X_r = \frac{\Delta H_t}{\Delta H_\infty} \quad (2)$$

where

$$\Delta H_t = \int_0^t (dQ / dt) dt$$

and

$$\Delta H_\infty = \int_0^\infty (dQ / dt) dt$$

dQ/dt is the heat flow. In practice ΔH_t corresponds to a partial area of the DSc curve between the onset of crystallization and a time t . The melting enthalpy ΔH_m is defined by equation (3b) integrated between the onset and completion of crystallization. The applicability of this model to crystallizing polymers has been discussed at some length by Hay²⁴. The rate constant, k contains information about the rates at

which nuclei form and crystals grow. Table 1 shows both the relationship between k and nucleation and growth parameters as interpreted by Evans ⁴⁵. In principle the morphology of the crystallites will be reflected in the integer values of n given in Table 1, hence n can be used to infer morphological information from calorimetric measurements.

CRYSTAL MORPHOLOGY	n	k	GEOMETRY
Sporadic spheres	4.0	$\frac{2}{3}\pi\dot{g}^3\dot{n}$	3-d
Predetermined spheres	3.0	$\frac{4}{3}\pi\dot{g}^3N$	3-d
Sporadic discs ^a	3.0	$\pi/3\dot{g}^2\dot{n}d$ ^c	2-d
Predetermined discs	2.0	$\pi\dot{g}^2Nd$	2-d
Sporadic rods ^b	2.0	$\pi/4\dot{g}\dot{n}d^2$ ^d	1-d
Predetermined rods	1.0	$\frac{1}{2}\pi\dot{g}Nd^2$	1-d

- a - of constant thickness, d .
 - b - of constant radius, d .
 - c - surface limited crystallization.
 - d - crystallization limited to a radius of d .
- ($\dot{n}, \dot{g}$ are the nucleation and crystal growth rate constants respectively and N is the density of nuclei)

Table 1: The physical interpretation of the Avrami parameters n and k (After Hay ²⁹).

The parameters n and k in what is generally referred to as the Avrami equation are typically derived from the slope and intercept respectively of linear plots of $\ln(-\ln(1-X_t))$ against $\ln t$. These plots have a tendency to curve yielding non-integer values of n . A number of explanations have been proposed to explain this non-linearity, some of which are discussed below. Alternatively n can be determined from the derivative of equation (1) and subsequently plotted as a function of time. An advantage of this method of determining n over the double log plot approach is that any changes in the value of n are immediately apparent. k can be calculated ⁴⁶ according to

$$k = \frac{\ln 2}{t_{1/2}^n} \tag{4}$$

where $t_{1/2}$ is the time taken for 50% of the total crystallization to occur.

The Avrami model assumes that spherulite growth ceases at the instant at which two growing centres impinge upon each other. This assumption is generally only valid during the initial part of the sigmoidal isotherm (primary crystallization). This limitation is often ignored and may be a contributory reason for the fractional exponents that appear in many publications.

There are reports in the literature of unexpected values of the Avrami index, e.g. Piccarolo et al.⁴⁷ found experimental evidence for the formation of at least two crystalline forms in a study of crystallization in high purity isotactic polypropylene. At high cooling rates a mesomorphic phase dominates the conversion of melt to solid with few spherulites being found whilst at lower rates crystallization is dominated by an α -monoclinic form. This phenomenon has also been observed by other authors⁴⁸. Between these two limits the two crystalline forms compete. This phenomenon will be difficult to model in the absence of very detailed knowledge of the physics of crystallization. The presence of two crystalline forms with different growth rates is not unusual in polymers, Lovinger et al.⁴⁹ studied the growth of α -monoclinic and β -hexagonal spherulites of iPP and found that the radial growth rate of the β form exceeded that of the α form at certain temperatures. Norton and Keller⁵⁰ also found that low crystallization temperatures favoured the growth of β -spherulites. Grubb and Yoon⁵¹ showed that α - and β -spherulites coexist in iPP and that under certain conditions one form can be transformed to the other.

Tobin⁵² proposed an alternative model similar in form to Avrami that contains two parameters i.e.

$$X_t = lt^n / (1 + lt^n) \quad (5)$$

where n and l have the same meaning as Avrami's n and k respectively. Tobins model is equivalent to that of Avrami for low degrees of conversion (<30%). Unfortunately this model has essentially been ignored although Martins and Cruz-Pinto⁵³ have compared the non-isothermal version with those of Avrami (equation (1)) and Malkin (equation (21)).

Increasing molecular weight⁵⁴ induces non-linearity in Avrami plots to occur at lower degrees of crystallinity. Molecular weight also has an inverse affect on the final degree of crystallinity reached at a particular temperature. This may have some implication for kinetic studies where polydisperse samples have been used, as molecular weight fractionation due to crystallization could contribute to non-linearity.

k has only a weak dependence on n and can be calculated according to Heiber⁵⁵ following

$$\ln(\bar{k}^{-n}(T)) = B_1 + B_2 T + B_3 T^2 \quad (6)$$

where the constants B_1 , B_2 and B_3 may be obtained by fitting a quadratic function to a master curve generated from published data. The temperature dependence of the crystallization half time $t_{1/2}$ is then given by

$$\frac{1}{t_{1/2}} = (\ln 2)^{-\frac{1}{n}} \exp[-(B_1 + B_2 T + B_3 T^2)] \quad (7)$$

Ziabicki⁵⁶ suggested a different empirical function to describe the temperature dependence of the crystallization half times where

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_{\max} \exp\left[-4 \ln(2) \frac{(T - T_{\max})^2}{D^2}\right] \quad (8)$$

and $(1/t_{1/2})_{\max}$, $T_{\max}$ and D are determined from regression analysis. However, some of these parameters can only be obtained with limited accuracy due to the difficulty in obtaining kinetics data over wide temperature range by DSC. Comparisons of Hieber's quadratic function⁵⁵ for describing the temperature dependence of $t_{1/2}$ (equation (7)) with that proposed by Ziabicki⁵⁶ suggests that the former gives a better fit to measured data^{48,57} than equation (8).

Khanna and Taylor⁵⁸ have suggested using a modified form of Avrami's function that is given by

$$Q_a(t) = \exp[-kt^n] \quad (9)$$

where Q_a is the fraction of *uncrystallized* polymer, n is the Avrami exponent and k is a kinetic constant.

Urbanovici et al.⁵⁹ have generalized Avrami's model and in doing so added an extra parameter, p where $p > 0$. The modified Avrami function is written as

$$X_r = 1 - [1 + (p-1)(kt)^n]^{1/(1-p)} \quad (10)$$

From equation (10) it is evident that as p tends to unity the function becomes increasingly similar to the Avrami model (equation (1)). Urbanovici et al.⁶⁰ have shown that equation (10) is slightly better at modelling the kinetic behaviour of poly(L-lactic acid) than equation (1). This is presumably due to the presence of the additional parameter.

Although Avrami's function and variations on it have been extensively used in the literature⁶¹⁻⁶³ alternative isothermal functions have been proposed. These models assume auto-catalytic reaction kinetics. Following this approach the first stage of crystallization involves the generation of nucleation sites. This is a time dependent process independent of temperature. The second stage involves the initiation of crystal growth at the nucleation sites. Sestak and Berggren⁶⁴ suggest that this can be described by

$$f(X_r) = X_r^m (1 - X_r)^n \quad (11)$$

where m and n are reaction order constants. This empirical relationship has been compared to Avrami's function (which has a physical basis) by Foreman and Blaine⁶² in a study of the crystallization behaviour of a number of materials including nylon-6, polyethylene, poly(ethylene terephthalate) (PET) and PEEK. Their findings show that both models were able to accurately model the experimental kinetics data.

3.3 NON-ISOTHERMAL CRYSTALLIZATION

Nakamura et al.⁶⁵ and Kamal and Chu⁶⁶ have modified the Avrami equation such that it can describe non-isothermal crystallization and both Patel and Spruiell⁴¹ and Chan and Isayev⁶⁷ have discussed these modifications in the light of process modelling. Many of the functions used to describe non-isothermal crystallization are derived by either integrating or differentiating the Avrami equation (equation (1)) to include a temperature dependent kinetic constant. Nakamura et al.⁶⁵ proposed an integral function of the form:

$$X_r = 1 - \exp \left[- \left(\int_0^t K(T) dt \right)^n \right] \quad (12)$$

which reduces to the Avrami expression under isothermal conditions when the non-isothermal crystallization rate constant $K(T) = k^{1/n}$ and n is the isothermal Avrami exponent. Patel and Spruiell⁴¹ utilised the differential form of Nakamura et al.'s integral expression

$$\frac{dX_r}{dt} = nK(T)(1 - X_r) \cdot \left\{ \ln \left[\frac{A}{(1 - X_r)} \right] \right\}^{\frac{(n-1)}{n}} \quad (13)$$

where the temperature dependence of Nakamura's rate constant $K(T)$ is given by

$$K(T) = J_o \exp \left[-\frac{U^*}{R(T - T_\infty)} - \frac{A(T_m^o + T)}{2T^2(T_m^o - T)} \right] \quad (14)$$

J_o and A are material parameters characteristic of a given polymer ⁶⁸. U^* is the activation energy for segmental jumping (see also equation (25)) and A is a thermodynamic constant. T_∞ is the temperature at which chain diffusion ceases and R is the gas constant.

Velisaris and Seferis ¹⁹ used a slightly different integral expression developed by Kamal and Chu ⁶⁶ given by

$$X_r = 1 - \exp \left[- \int k(T) n t^{n-1} dt \right] \quad (15)$$

to model non-isothermal crystallization of poly(ether ether ketone) (PEEK). Differentiating this expression yields ⁶⁹

$$\frac{dX_r}{dt} = nk(T)(1 - X_r)t^{(n-1)} \quad (16)$$

and at constant temperature integration of this expression yields the Avrami equation.

Nakamura's model has been criticized since it only contains a single kinetic parameter ⁷⁰ whereas crystallization is a two stage process composed of the nucleation of spherulites followed by their growth. Unfortunately these two processes have different dependencies on temperature, pressure and shear stress. The original model makes no allowance for the induction time for nucleation to occur. Thus Chan and Isayev ⁶⁷ were unable to describe their data using the Nakamura model. To overcome this problem without including a specific induction time they used the time corresponding to the lowest measurable crystallinity value as a starting condition for the differential form of the function. This deficiency has been addressed by Sifleet et al. ⁷¹ and others. Sifleet et al. proposed using a non-isothermal induction time t_{ni} that is given by a summation of isothermal induction times t_i i.e.

$$= \int_0^{t_{ni}} \frac{dt}{t_i(T)} = 1 \quad (17)$$

where $\bar{t}$ is the induction time index. $t_{ni}(T)$ is given by the value of the upper limit of the integral when the dimensionless unit $\bar{t}$ is unity. Chan and Isayev⁶⁷ demonstrated a good agreement between predicted induction times and experimental data for PET derived from DSC measurements. They suggested that isothermal induction times could have an Arrhenius temperature dependence such that

$$t_i = t_c \exp(T_0 / T) \quad (18)$$

where t_c and T_0 are temperature independent material constants. Godovsky and Slonimsky⁷² proposed an alternative description of $t_i(T)$ for melt crystallization where $t_i = t_m (T_m^0 - T)^{-a}$ where a and t_m are constants independent of temperature. For fast crystallizing materials such as iPP the induction time is often so short that it cannot be accurately determined⁶⁷. In addition the final degree of crystallinity often depends on the cooling rate which cannot be modelled by the Nakamura function⁴⁸.

Ozawa's model⁷³ following Evans⁴⁵ is of the form

$$X_r = 1 - \exp\left[-\frac{\kappa(T)}{\phi^n}\right] \quad (19)$$

This function contains a temperature dependent rate constant κ and a cooling rate ϕ where $\phi \equiv -\partial T / \partial t$. The parameter n as in the Avrami model represents the morphology of the crystals and can be determined for a constant cooling rate. The usefulness of Ozawa's function has been questioned⁴¹ since it requires knowledge of the relative crystallinity at different temperatures whereas in practice crystallinity data can only be obtained over limited ranges of temperature for a narrow band of cooling rates. This function also assumes a constant cooling rate and therefore is of limited use in modelling crystal growth rates during injection moulding. Interestingly Hieber⁵⁵ has shown that Nakamura's model is equivalent to Ozawa's function under conditions of constant cooling. Despite these reservations Edes and Wlochowicz⁷⁴ found that this model accurately described their kinetics data obtained from the crystallization of iPP.

There is evidence to suggest⁷⁵ that most kinetic models fail when X_r reaches values of 0.7-0.8 due to spherulite impingement. Secondary crystallization that continues to occur beyond this limit, albeit at a

much slower rate, is not catered for by the above models. To accommodate secondary crystallization Dietz⁷⁶ proposed a model where

$$\frac{dX_r}{dt} = nk(T)(1 - X_r)t^{n-1} \exp\left[-\frac{aX_r}{1 - X_r}\right] \quad (20)$$

In this function $X_r = X(t)/X_\infty$ and a is a scaling parameter varying from 0 to 1.

Malkin et al.'s model^{24,77}, unlike those previously described, cannot be reduced to the Avrami equation. Malkin et al.'s empirical model is given by

$$dX_r / dt = K_m (X_{eq} - X_r)(1 + C_0 X_r) \quad (21)$$

where K_m and C_0 are temperature dependent parameters. X_r is the degree of crystallinity and X_{eq} is the maximum degree of crystallinity that develops over a long period of time. The model requires five parameters to describe the temperature dependence of crystal growth. Martins and Cruz-Pinto⁵³ compared the theoretical predictions of Malkin, Nakamura and Tobin (suitably modified to the non-isothermal condition) with non-isothermal data for poly(oxymethylene) (POM) and PEEK. Their findings show that Tobin's two parameter model⁵² provides a fit of comparable quality to that obtained using the five parameter Malkin function which is better than that provided by Nakamura's function⁶⁵. Paiz et al.⁷⁸ compared the Nakamura and Malkin functions in a study of the effect of nucleating agents on the non-isothermal crystallization of iPP by DSC. Fits to the kinetics data using Nakamura's model were poor in contrast to those obtained using Malkin's function. This observation is contrary to the findings of other workers⁷⁹.

Shoeborn and Haessner⁸⁰ using an activation energy approach developed a method for interpreting non-isothermal kinetics data in terms of nucleation and growth rates. Fan-Chiang et al.^{81,82}, following Icenogle⁸³, have shown that the number of nuclei $\bar{N}(t)$ appearing in a melt over a period of time

between $\bar{t}$ and $\bar{t} + d\bar{t}$ depends on the rate at which it is cooled and the remaining fraction of material that

can be crystallized $\left[1 - X_r(\bar{t})\right]$ i.e

$$\bar{N}(\bar{t}) = \int_0^{\bar{t}} \left. \frac{dM}{dT} \right|_{T=T(\bar{t})} \cdot \left. \frac{dT}{dt} \right|_{t=\tau} [1 - X_r(\bar{t})] d\tau \quad (22)$$

where $\bar{t}$ is the time at which nuclei first appeared.

The volume of spherulites $V(t, \tau)$ growing in the melt is given by

$$V(t, \bar{t}) = (4/3)\pi \left[\int_0^t G_r[T(u)] du \right]^3 \quad (23)$$

where u is a dummy time variable. Equations (22) and (23) can be combined^{81,82} to produce a general model for describing the time dependence of the fractional crystallinity as a function of cooling rate where

$$X_r = 1 - \exp \left\{ -\frac{4}{3}\pi \int_{t_0}^t \left[\int_{\bar{t}}^t G_r[T(u)] du \right]^3 \frac{dM}{dT} \Big|_{T=T(t)} \cdot \frac{dT}{dt} \Big|_{t-\bar{t}} d\bar{t} \right\} \quad (24)$$

t_0 is the elapsed time between cooling the melt from a temperature T_i to the equilibrium melting point T_m^0 . dM/dT is the change in the potential density of nuclei with temperature. Equation (24) predicts that the rate of nucleation and the spherulite growth rate will increase with increasing cooling rate up to a limiting value that for iPP is approximately 400 K min^{-1} . This increase in nucleation rate induces a proliferation of small spherulites that is consistent with experimental observations^{81,83}.

In practice melt or cold crystallization data for most polymers can only be obtained over limited temperature ranges. To extend this range extrapolation procedures have been employed^{41,67} that use Hoffman et al.'s¹⁵ relationship between the linear growth rate of spherulites G_r and the temperature at which the material crystallizes i.e.

$$G_r = G_0 \exp \left(-\frac{U^*/R}{T - T_\infty} \right) \exp \left(-\frac{K_g}{T \Delta T f} \right) \quad (25)$$

where G_0 is a pre-exponential factor. The first exponential term in the model accounts for the increase in melt viscosity and hence lowering of molecular mobility that occurs as the crystallization temperature approaches T_∞ . T_∞ is a hypothetical temperature where chain motion due to viscous flow or reptation ceases and is assumed to be equivalent to $T_\infty = T_g - 30 \text{ K}$. The second exponential term represents the driving force for crystallization. This term is dominated by the degree of supercooling given by

$\Delta T = T_m^0 - T$ where T_m^0 is the melting point at equilibrium. The opposing temperature dependencies of these two exponential terms gives rise to a peak in a plot of crystal growth rate against temperatures as shown in Figure 4. This peak is typical of nucleation controlled processes. The location of the maximum growth rate is midway between the thermodynamic melting point, T_m^0 and T_g . U^* is the activation energy for segmental jump rate in polymers that according to Hoffman can be assigned a value of 6284 J/mol. and R is the gas constant. The parameter $f = 2T / (T + T_m^0)$ is a corrective term⁸⁴ that approximately describes the decrease in the latent heat of fusion that occurs on lowering the crystallization temperature.

Equation (25) has been modified by both Chan and Isayev⁶⁷ and Patel and Spruiell⁴¹ such that the growth rate G_r is replaced by $(1/t_{1/2})$ and G_o by $(1/t_{1/2})_o$ where $1/t_{1/2}$ is the reciprocal of the time taken for 50% of the crystallinity to occur. Substituting this term for the growth rate of spherulites provides a means of positioning plots of % crystallization against temperature on the temperature axis. K_g is a function of the surface free energy of the crystals and of the heat of crystallization. Both K_g and $(1/t_{1/2})_o$ can be obtained from a plot of $\ln(1/t_{1/2}) + U^*/[R(T - T_\infty)]$ versus $1/(T\Delta T.f)$.

Following Hoffman et al.'s approach to modelling spherulite growth rates several authors have suggested that the Avrami rate constant could also possess a similar temperature dependence^{19,41,85,86} i.e.

$$k = k_o \exp\left[-E / R(T - T_\infty)\right] \exp\left[-C / (T.\Delta T.f)\right] \quad (26)$$

although the factor f is often omitted. E and C are material dependent parameters. Similarly it follows that the induction time t_i could also possess an equivalent temperature dependence. Maffezzoli et al.⁸⁶ pointed out the fact that some of the physical significance of the parameters will be lost in applying a model developed for microkinetics to macrokinetic data. They suggest for example that the induction time could depend on temperature according to

$$t_i = k_{i0} \exp\left[-E_{i2} / R(T - T_g)\right] \exp\left[-E_{i1} / (T_m^0 - T)\right] \quad (27)$$

where k_{i0} , E_{i2} and E_{i1} are constants that are determined by fitting the equation to isothermal data measured at a number of temperatures. A similar relationship can be used to describe the temperature dependence of k . Good agreement was obtained between isothermal and non-isothermal kinetics data by Maffezzoli et al. using a combination of the Nakamura model together with the temperature dependencies of k and t_i (equations (26) and (27)).

3.4 PRESSURE EFFECTS

The effect of pressure on crystallization kinetics has received scant attention in the literature. This presumably is a reflection of the experimental difficulties associated with measurements of this type. Ito et al.^{70,87} demonstrated the importance of pressure on crystallization kinetics in iPP. Their results show that increasing the pressure from atmospheric to approximately 400MPa suppresses the rate at which spherulites grow and shifts the temperature range in which crystallization occurs to higher values.

Several models have been proposed that contain pressure sensitive parameters^{70,87,88}. Ito et al.^{70,87} extended a model based on a non-isothermal Avrami function⁸⁹ to account for the pressure dependence of the nucleation and growth rates. In this model the degree of transformation X_r at time t is given by

$$-\ln\left(1 - \frac{X_r(t)}{X_\infty}\right) = \frac{1}{X_\infty} \cdot \frac{\rho_c}{\rho_l} \int_0^t v(t, \bar{t}) \dot{n}(\bar{t}) d\bar{t} \quad (28)$$

for homogenous nucleation. The corresponding function for heterogenous nucleation is of the form

$$-\ln\left(1 - \frac{X_r(t)}{X_\infty}\right) = \frac{1}{X_\infty} \cdot \frac{\rho_c}{\rho_l} \left[\int_0^t \frac{d\bar{N}(\bar{t})}{d\bar{t}} v(t, \bar{t}) d\bar{t} + \bar{N}(0)v(t, 0) \right] \quad (29)$$

where $v(t, \bar{t}) = k_f \left| \frac{d\bar{N}(\bar{t})}{d\bar{t}} \right|^n$ and X_∞ is the final degree of crystallinity at long times. $G(u)$ is the

linear spherulitic growth rate at time u . $\dot{N}$ is the nucleation rate at a time $\bar{t}$. The number of nuclei at some time $\bar{t}$ is given by $\bar{N}(\bar{t})$. n is the Avrami index and k_f is a shape factor which for a sphere is $4\pi/3$. The densities of the crystalline and melt phases are given by ρ_c and ρ_l respectively. The ratio ρ_c/ρ_l can be taken as constant. Ito et al.^{70,87} extended Takayanagi and Kusumoto's expressions⁹⁰ to include the temperature dependency of G and to incorporate pressure and shear stress dependencies for n .

3.5 SHEAR-INDUCED CRYSTALLIZATION

Shear-induced crystallization is that which occurs in, for example, the surface layers of extruded pipe or injection moulded articles⁹¹. A related phenomenon is associated with elongational flow that is responsible for the fibrillar nature of spun fibres. The influence of shear stress on the crystallization behaviour of polymers has been recently reviewed by Eder et al.⁹². During injection moulding the melt is subjected to high shear stresses leading to the growth of one-dimensional crystals near the mould wall^{93,94}. This shear-induced skin layer covers a core of molten material that in most cases is relatively

unstressed and in which crystals grow in three-dimensions. The presence of a thick skin layer can cause undesirable effects such as stress-whitening, warpage or brittleness⁹⁵⁻⁹⁷. Skin layers can be reduced to some extent by using narrow molecular weight distribution, rheology controlled grades rather than reactor feedstocks⁹⁸.

After the cessation of flow the amount of shear-induced orientation that remains in the melt is balanced by the amount of molecular relaxation that occurs. The rheology of polymer melts can be very sensitive to the presence of small percentages of high molecular weight polymers. Janeschitz-Kriegl et al.⁹⁹ studied the temperature dependence of relaxation times on temperature in polypropylene melts through double logarithmic plots of birefringence against time. The relaxation times derived from the slopes of these plots, when plotted as a function of the zero shear viscosity, showed that over a range of 20 °C the zero shear viscosity increased by a factor of 2 whilst the relaxation time increased by a factor of 70. Based on this type of experimentation Janeschitz-Kriegl et al.⁹⁹ proposed a probability function, ϕ for the occurrence of shear induced crystallization. The probability function of the form

$$\tau \dot{\Phi} = (\dot{\gamma} / \dot{\gamma}_a)^2 (1 - \phi) - \phi \quad (30)$$

contains a growth term controlled by a critical shear rate $\dot{\gamma}_a$ and a decay term governed by the relaxation time τ . The ratio of the shearing time t_s to τ is small at temperatures at which shear-induced crystallization occurs due to the magnitude of the relaxation time. Thus for short times equation (30) becomes

$$\Phi(\dot{\gamma}, t_s) = (\dot{\gamma} / \dot{\gamma}_a)^2 t_s / \tau \quad (31)$$

Janeschitz-kriegl et al.⁹⁹ found that this simple model generated promising fits to isothermal PP data.

4. SIMULATION OF INJECTION MOULDING

Crystallization begins during the filling stage of injection moulding where the melt is subject to rapid cooling, high pressure and shear stress. Thus the models that describe crystallization kinetics should in principle contain temperature, shear stress and pressure dependent parameters. However it may be possible to simplify such calculations depending on the sensitivity of crystallization to these parameters i.e. temperature effects may be negligible in comparison with the influence of pressure or shear stress.

Models for crystallization should also take into account the presence of nucleating agents that accelerate the rate at which crystallization occurs.

Simulations of crystallization occurring during injection moulding are limited^{93,100-102} and are typically based on modelling the time dependent transfer of heat from the material in the mould cavity to the mould wall. Kamal and Lafleur^{101,102} utilized a model for heat transfer that included Nakamura's description of non-isothermal crystallization kinetics. Hieber and Chang¹⁰³ employed a temperature dependent specific heat to accommodate the heat of fusion resulting from crystallization of polypropylene during the filling and packing phases of moulding. Manzione¹⁰⁴ developed an empirical relationship for describing a crystallinity profile through a cross-section of a moulding. The models used by Hieber and Chang¹⁰³, Manzione¹⁰⁴ and Kamal and Lafleur^{101,102} did not take into account the shear induced crystallinity that occurs in the interface region between the mould wall and the melt, due to the dearth of available models. More recently Hsiung and Cakmak¹⁰⁵ modified Nakamura's function to include empirically modelled stress and temperature dependent parameters. This modification allows non-isothermal crystallization to be modelled in strained fluids. Their work showed a decrease in the induction time and an increase in the rate of crystallization with increasing shear stress that has been observed by other workers¹⁰⁶⁻¹⁰⁸

Isayev et al.'s model^{67,93} allows either quiescent or shear induced crystallization to occur at any point within the mould cavity. The 'type' of crystallization that occurs depends on whether or not shear induced crystallization can occur within the induction time period of quiescent crystallization. While their predicted pressure traces during mould filling were in good agreement with those obtained in practice there was some disparity between comparable traces for the packing and freezing phases of moulding. Isayev et al. have suggested that these differences are due to their treatment of the melt as an elastic rather than as a viscoelastic fluid and problems with measurement difficulties respectively. Microscopy studies showed good agreement between the measured and predicted thicknesses of the shear induced skin layer. Using equations (28, 29) with temperature, shear stress and pressure dependencies of the rates of nucleation, crystal growth ($\dot{n}, \dot{G}$ respectively) and the number of nuclei ($\bar{N}$) Ito et al.⁷⁰ calculated the time dependent crystallization of iPP through the thickness of a rectangular plate moulding. Values for the temperature, shear stress and pressures for each level through the moulding were calculated using injection moulding software during mould filling, packing and cooling. Simulations of crystallization at two different injection speeds showed some interesting morphological behaviour that agreed with that observed in practice. Crystallization began during mould filling although it proceeded slowly in the surface regions of the melt that were in contact with the mould surface due to substantial supercooling. In the layer beneath the skin the crystallization rate was found to be much

higher. In fact crystallization in this layer was the fastest observed in traversing the thickness. This is due to a combination of the relatively high temperatures and shear stresses experienced by the melt close to but not at the interface with the cavity wall. Crystallization in the core regions of the melt showed two stages of growth. Initially growth of spherulites was suppressed by the progressively increasing pressure experienced by the melt towards the end of the filling phase. Subsequently this high pressure fell during the packing/cooling phases of moulding causing an acceleration of the crystal growth rate $\dot{G}$

Hsiung and Cakmak¹⁰⁹ modelled crystallinity gradients that develop during the injection moulding of slowly crystallizing polymers such as poly(phenylene sulphide) and poly(aryl ether ketones). In their model they modified the specific heat capacity of the polymer to account for the heat evolved during crystallization. The crystallization process itself was modelled using Nakamura's function, suitably modified to account for an induction time by adjusting the lower limit of the integral term to that at which crystallization began. The 'induction' time was allowed to have a parabolic dependence on temperature and have a rate dependence on temperature. This enabled the reduction in induction time that occurs with increasing shear stress to be modelled. A similar dependence on temperature and shear stress was used for Nakamura's rate constant, K . The Avrami exponent also has to depend on the shear stress since flow fields affect spherulitic morphologies. Generally good agreement between the predicted morphology and that observed in practice was obtained i.e. the relationships between skin and core thicknesses as a function of injection speed, mould temperature and crystallinity gradients. Interestingly the model also predicted that the material would be essentially amorphous when moulded using a combination of low injection speeds and mould wall temperature. This behaviour was observed in practice.

5. THE USE OF MASTER CURVES

The concept of a master curve to describe crystallization kinetics is very appealing given the number of variables such as molecular weight, polydispersity, cooling rates and crystallization temperature that are possible. In particular this type of curve can be used to predict material properties over a wider range than those accessible by experimentation. A number of authors have generated master curves for isothermal data^{73,110-118} although there has been less activity in producing master curves for non-isothermal data^{73,116-121}

Hieber⁵⁵ used published data for iPP and PET and used the inter-relationship between the parameters in the Avrami, Ozawa and Nakamura models to generate master curves. Whilst the master curves for iPP showed good superposition for data obtained under both isothermal and non-isothermal conditions, those for PET were less satisfactory. Poor superposition of the PET data may reflect a molecular weight

dependence of the kinetics ¹²²⁻¹²⁴ although Van Antwerpen ¹²³ claims that crystallization behaviour is independent of molecular weight above some critical value. Furthermore Jackson et al. ¹²² and Jabarin ¹²⁴ have shown that residual catalyst present in PET can have as much influence over the kinetics of crystallization as variations in molecular weight. Despite the lack of superposition of PET data the master curves for both materials can be described by quadratic functions relating the rate of crystallization to temperature for both isothermal and constant cooling rate conditions.

Chan et al. ^{75,121} developed a procedure for superimposing kinetics data that does not rely on a model for its success. This assumes that

$$\frac{dX_r}{dt} = F(T, X_r) = Z(T)f(X_r) \quad (32)$$

which relates the rate of change of the degree of crystallinity, X_r to a crystallization temperature T through a temperature dependent crystallization constant Z . Whilst it is not necessary to know the details of $Z(T)$ or $f(X_r)$ it is necessary to know the temperature dependence of Z . Using this procedure Chan et al. constructed a master curve for both isothermal and non-isothermal kinetics data for PET ⁷⁵. The shift factors obtained during the construction of the master curve can be used to compare those derived from other means using specific kinetic models. Chan et al. ¹²¹ also derived a master curve that is a good approximation for non-isothermal kinetics data obtained from polypropylene samples of differing molecular weight. This suggest that the kinetics of crystallization in polypropylene are insensitive to an eight-fold change in molecular weight, confirming the findings of Hieber ⁵⁵.

6. THE INFLUENCE OF ADDITIVES ON CRYSTALLIZATION BEHAVIOUR

6. NUCLEATING AGENTS

Additives that act as nucleating agents are often added to feedstocks used in injection moulding to accelerate crystallization and therefore reduce cycle times ^{14,85,125}. Reinforcing fibres added to polymer matrices can also induce crystallization ^{86,126} and may alter the crystal morphology and suppress crystallinity by sterically hindering crystal growth ¹²⁷⁻¹²⁹. This heterogenous nucleation has a temperature dependence and its effect can be seen in isothermal DSC experiments as an induction time prior to crystallization, noting that induction times are not easily detected in non-isothermal experiments. Maffezzoli et al ⁸⁶ have suggested that the induction time should be incorporated into crystallization models to enable them to satisfactorily predict crystallization behaviour. This suggestion has been challenged by Chan and Isayev ⁶⁷ who attributed the disparity between predictions made using the

differential form of the Nakamura model and DSC data to thermal lag between the sample and the calorimeter. Chan and Isayev ⁶⁷ demonstrated the validity of their thesis by showing that corrections to Nakamura's function to include an induction time were of minor significance in describing the crystallization behaviour of nylon-6 in comparison with changes in the experimental data to account for thermal lag effects.

Narh et al. ¹³⁰ have demonstrated the role that nucleating agents play in determining the rate of crystallization and the textures that are developed in commercial samples of polyethylene. Some of the samples were dissolved in boiling xylene and filtered using filters of differing degrees of coarseness to remove any insoluble nucleating agents present. In other specimens the density of nuclei was increased by adding potassium stearate of known grain size. This resulted in less supercooling, increased lamellar thickness within the spherulites, higher crystallization temperatures and higher melting points.

Iroh and Berry ^{131,132} in a study of the effects of a nucleating agent (sodium benzoate) on the mechanical properties of polypropylene analysed kinetics data using the Avrami equation (Figure 5). Their results showed that the addition of 0.5wt% sodium benzoate to polypropylene increased the crystallization rate by ~50%. This enhanced rate of crystallization was however significantly less than that which resulted after the addition of 30wt% glass-fibres that more than doubled the crystallization rate in comparison with that measured for unfilled non-nucleated polypropylene. Interestingly adding sodium benzoate to the glass filled material had a negligible effect on the rate at which the material crystallized.

Paiz et al. ⁷⁸ studied the influence of sodium benzoate, sodium sulphate, titanium dioxide and aluminium benzoate on the non-isothermal crystallization kinetics of iPP using DSC. Both sodium benzoate and aluminium benzoate (at concentrations of 2 wt%) increased the peak crystallization temperature (Fig. 4) by 10-20 °C. In contrast shifts in the peak temperature ranging from 1-5 °C were observed using the less effective nucleating agents titanium dioxide and sodium sulphate.

6.2 PIGMENTS

Certain organic pigments such as blue or green phthalocyanins possess good technological properties such as high colouring power and colour fastness in addition to being stable at the elevated temperatures experienced during processing. The low production cost of these materials makes them particularly attractive to plastics processors. However problems of product distortion can occur in large articles moulded from plastics such as HDPE when coloured by these pigments. This distortion is due to the residual stresses that develop within the mouldings. These occur because of changes in the crystallization behaviour of the material resulting from the nucleating effects of the pigments ¹³³. Similar

problems are also encountered with other types of organic pigment such as perylenes or diazo compounds.

Both organic and inorganic pigments are used singly or as mixtures to colour plastics at concentrations ranging from 0.1-2%. The presence of these colourants can significantly affect both the dimensional stability and the mechanical properties of mouldings^{134,135} by acting as nucleation agents^{136,137} causing changes in the crystallization behaviour of the host polymer^{138,139}. Kersting et al.¹⁴⁰ showed that the addition of pigments can improve the notched Izod impact properties of medium and high impact heterophasic polypropylene copolymers. Although interestingly their study revealed that the improved mechanical behaviour was due to the presence of the pigment carrier (either polyethylene or wax) rather than the pigments themselves (titanium dioxide or phthalocyanin blue). In contrast Ritter¹⁴¹ showed that the presence of titanium dioxide at concentrations of 0.3% and 5% had comparable adverse affects on the mechanical properties of polyethylene. However it is not clear from this study whether or not the influence of the pigment carrier on mechanical performance was explored. Nagy and White¹⁴² in a study of the factors affecting the shrinkage of rotomoulded polyethylene parts while using a range of different pigments and processing conditions discovered that the surfactant used to disperse the dry blended pigment increased warpage by approximately a factor of 2 and shrinkage by almost 30%. The surfactant, zinc stearate was used at a concentration of 0.077wt%.

Dolgopolsky et al.^{39,143} studied the influence of pigments on the crystallization kinetics and mechanical properties of polypropylene as a function of concentration. The pigments used in their study were irgazin yellow (tetrachloroisindolinone), hostaperm red (2,9-dimethylquinacridone) and chromophthal green (Cu-phthalocyanin) at concentrations of 0.1, 0.5 and 1.0%. The isothermal kinetics data obtained by DSC data was interpreted using a modified Avrami function (equation (9))³⁹. Whilst all of the pigments enhanced the amount of crystallinity in comparison with that of the unpigmented material, hostaperm red proved to be the most active nucleating agent increasing crystallinity by approximately 7%. This effect was found to be essentially independent of the pigment concentration. Interpreting the kinetics data in terms of equation (17) showed that the thickness of the crystal lamellae was enhanced by the presence of the pigments and in particular by chromophthal green. Changes in the equilibrium melting temperature and in the latent heat of fusion¹³⁸ suggest that the morphology of the crystals changes with increasing concentration of hostaperm red from the α - monoclinic form to a β - pseudohexagonal form.

Tuturro et al.¹⁴⁴ demonstrated the nucleating effects of a number of organic pigments including phthalocyanins, perylene, anthraquinone and diazo compounds in high density polyethylene (HDPE). The presence of the organic dyes increased the rate at which the HDPE crystallized and was shown to depend on the concentration of copper phthalocyanin. Interestingly the pigments did not affect the absolute level

of crystallinity implying that these compounds affect only the kinetics of crystallization and not the thermodynamics of the material. Comparisons of the kinetics of crystallization with those of inorganic dyes e.g. cadmium selenide and a blend of lead compounds (sulphate, chromate and molybdate) showed that the inorganic materials had no effect on crystallization kinetics

7. CONCLUSIONS

Functions used to model the kinetics of crystallization in polymers stem from two origins - the physically based model of Avrami ⁴⁴, Kolmogoroff ⁴² and Johnson and Mehl ⁴³ or the empirical relationship proposed by Malkin ^{24,77}. These root functions have been extended by a number of authors to account for their data and to extend their range of applicability to account for factors such as induction times or non constant cooling rates.

From the literature it is evident that the agreement between the models and experimental data is somewhat dependent on the measurement method, for example, there is evidence to suggest that results obtained from dilatometry do not match those obtained from DSC. Furthermore there seems to be no consensus of opinion regarding the correction of DSC data to account for thermal lag to enable comparison of data obtained at different cooling rates. This has been demonstrated by Chan and Isayev ⁶⁷ who obtained an improvement in a fitting theory to experimental data by assuming an alternative correction procedure.

Whilst there is no doubt that certain pigments can accelerate the rate at which some polymers crystallize there is some evidence to suggest that the carriers used to disperse the pigment in the polymer may be acting as a nucleating agent rather than the colourant itself ¹⁴².

From the literature it is also apparent that inferring the morphology of crystallizing melts through the numerical values of parameters in crystallization models is unreliable. This can be illustrated by considering the interpretations proposed by various authors to explain the non-integer values of the shape parameter, n derived from Avrami plots. These are typically derived from slightly curved plots. Various explanations have been proposed to explain this non-linearity including the presence of different shapes or types of spherulite, polymorphism, molecular weight fractionation or spherulite impingement. In the absence of direct microscopical investigation it is very difficult to say which of these interpretations is most appropriate. Thus where possible calorimetric information should be supported by microscopy.

8. NOMENCLATURE

- G_r = linear growth rate for spherulites
 ΔH_t = heat evolved over a limited period of time, t due to crystallization (Equation (2))
 ΔH_∞ = heat evolved over a long period of time, t due to crystallization (Equation (2))
 T = temperature (C or K)
 t = time (s)
 k = Avrami rate constant
 n = Avrami index
 X_r = relative crystallinity
 K = temperature dependent Nakamura rate constant
 ϕ = constant cooling rate (Ozawa equation)
 K_m = temperature dependent parameter- Malkin equation
 C_o = temperature dependent parameter- Malkin equation
 T_∞ = hypothetical temperature at which all motion associated with viscous flow or reptation ceases
 T_g = glass transition temperature (K)
 T_m^o = equilibrium melting point of crystals (K)
 ΔT = degree of supercooling (K)
 ΔG_f = Gibbs free energy
 G_c = Gibbs free energy of a crystal
 G_m = Gibbs free energy of a melt
 ΔH_f = Latent heat of fusion
 ΔS_f = Difference in entropy between molecules in a melt and in a crystal
 G_o = pre-exponential factor in Hoffmann, Davis, Lauritzen model
 U = activation energy for chain motion (reptation) in the melt
 R = gas constant
 K_g = represents the surface free energy of crystals and the heat of crystallization in the Hoffmann, Davis, Lauritzen model.
 f = a correction factor that accounts for the dependence of the heat of fusion on temperature
 T_c = crystallization temperature
 m = reaction order constant in Sestak-Bergan (equation (11))
 n^* = reaction order constant in Sestak-Bergan (equation (11))
 t_{ni} = non-isothermal induction time (equation (17))
 t_i = isothermal induction time (equation (17))
 $\bar{t}$ = induction time index (equation (17))
 t_m = material constant in the Godovsky-Slonimsky function.
 a = material constant in the Godovsky-Slonimsky function.
 $K(T)$ = non-isothermal Avrami rate constant (equation (12))
 T_o = material constant (equation (18))
 t_c = material constant independent of temperature (equation (18))
 $N.$ = nucleation rate (equation (28))
 $G.$ = crystal growth rate (equation (28))
 N = density of nuclei (equation (28))
 $\bar{N}$ = number of nuclei (equation (29))
 k_f = shape factor
 ρ_c = crystal density
 ρ_e = melt density
 Z = crystallization rate constant (equation (32))
 K = Ozawa crystallization rate constant
 t_o = period of time between cooling from a temperature T_i to T_m^o
 M = potential density of nuclei
 V = volume of spherulites growing in a melt

- D = material constant (equation (8))
 K = growth rate constant (equation (A2-3))
 G_o = growth rate constant (equation (A2-3))
 C_r = cooling rate (equation (A2-3))
 a = scaling parameter (equation (20))
 J_o = thermodynamic constant (equation (14))
 A = material constant (equation (14))
 $\dot{\phi}$ = probability function for equation (30)
 $\dot{\gamma}$ = shear rate
 $\dot{\gamma}_a$ = critical shear rate of activation (equation (30))
 τ = relaxation time (equation (30))
 t_s = shearing time

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11. APPENDIX 1: EXPERIMENTAL CONSIDERATIONS

Whilst this review is mainly concerned with modelling crystallization kinetics in polymers many of the comparisons between theoretical predictions and experimental observations rely on correction factors that were applied to the experimental data ^{145,146}. There are examples within the literature of cases where theoretical fits to experimental data were significantly improved as a result of modifying the data by using a different factor to that used by the original authors ⁶⁷. These corrections are particularly important for non-isothermal DSC measurements to compensate for the thermal lag between the sample and the calorimeter. Not surprisingly they are particularly important at high cooling rates. Isothermal data may also require some adjustment if there is some uncertainty over how rapidly the sample can be cooled until it reaches the measurement temperature. Isothermal DSC measurements can be subject to overshoots in temperature if fast cooling rates are used. The significance of such an overshoot will depend on the material being studied but will have a minimal effect in slow crystallizing materials such as PET.

For these reasons small samples (8-12 mg) are used in DSC studies. Using small samples will help to ensure that the sample temperature is uniform throughout: as incomplete melting can give rise to large errors in crystallization kinetics measurements due to the presence of residual crystallites. Typically, small discs of material of comparable diameter to a DSC pan are cut from thin sheets of compression moulded material to facilitate heat transfer between the specimen and the calorimeter.

Details of the procedures used to analyse DSC data have been described elsewhere ^{54,147}. The technique itself can only be used over limited ranges of temperature. In isothermal experiments at high temperatures, near the crystal melting point, the rate of crystallization becomes very slow and difficult to monitor. In contrast, at lower temperatures the rate of crystallization is too fast. In this case rapid crystallization begins to occur during cooling and is often superimposed on the DSC overshoot. This loss of peak definition introduces a significant error into the analysis of peak area.

It is possible to obtain both isothermal and non-isothermal kinetics data from some polymers from cold crystallization measurements made over a narrow temperature ranges. However for fast crystallizing materials such as polyethylene such data is extremely difficult to obtain as these polymers crystallize during fast quenching from the melt to some temperature below the glass transition temperature.

Michel ¹⁴⁶ showed the influence that the melt's thermomechanical history has on crystallization kinetics for isotactic polypropylene. Melt memory can have a stronger influence on crystallization kinetics than both tacticity or influences of molecular weight. Subjecting the melt to shearing forces seems to be the most effective way of removing melt memory whilst compression moulding appears to be the most

ineffectual process. Experimental studies of shear-induced crystallization generally involve monitoring the influence of shear on the the induction time of crystallization using rotational rheometers^{92,148,149} where the onset of crystallization is seen as an increase in torque. Other studies monitored crystal growth through changes in volume¹⁵⁰ or as the number of nuclei formed during shearing^{92,151}. Tribout et al.¹⁵² studied the appearance of nuclei and subsequent growth of crystals as a function of shear history in ethylene-propylene block copolymer using polarised light microscopy. The rate at which crystals grow can be deduced by measuring the intensity of transmitted light as a function of time and expressing it as a ratio with respect to the 'final' light intensity at the end of the measurement period. Such studies are typically carried out under isothermal conditions, although non-isothermal measurements have been carried out e.g. Wolkowicz¹⁵¹. Narh et al.¹⁵³ studied the combined influences of temperature, shearing time and shear stress on the crystallization behaviour of strained melts of PET. Their results showed the existence of an induction time for stress induced crystallization that decreases with both increasing shear rate and temperature.

Optical microscopy can be used to measure the growth rate of spherulites. The initial structure of a spherulite (often referred to as a quadrite) is a small quasi 2-dimensional rectangular array of cross-hatched lamellae. Quadrites can be very small i.e. $<6 \mu\text{m}$ ¹⁵⁴ in materials such as iPP and therefore measurements of the growth rate of the spherulites are difficult using microscopy techniques. In practice it is possible to determine the growth rates of objects with initial diameters of 6-10 μm are possible using polarized light microscopy. The time taken for growing spherulites to impinge on each other will obviously reflect their rate of growth. Measurements of spherulitic growth rates in melts containing nucleating agents are experimentally more difficult to make due to the enhanced number of spherulites and rate of crystallization. Spherulitic growth rates in ($\mu\text{m}/\text{min}$) obtained from the dependence of spherulite radius against time can be used to extract kinetic information and to generate values for surface energies using Lauritzen - Hoffmann theory¹⁵⁵⁻¹⁵⁷.

Many polymers have been analyzed with regard to spherulite growth. A plot of growth rate against temperature is bell-shaped (Figure 4) and decreases in intensity with increasing molecular weight. The shape of this plot can be described by

$$\ln(G / G_{\max}) = f(T - T_{\infty}) / (T_m - T_m^o) \quad (\text{A1.1})$$

where $G_{\max}$ is the maximum rate of crystallization, T_m^o is the thermodynamic melting temperature and T_{∞} is around 50C below T_g .

Dilatometry is commonly used to study crystallization kinetics especially for crystallization studies involving extensive supercooling ¹⁷. Unfortunately this technique cannot be used to study high rates of crystallization because material begins to crystallize before thermal equilibrium is established. Other less common techniques are available to study crystallization behaviour that include x-ray diffraction ^{158,159}, Raman spectroscopy and Fourier transform infra-red spectroscopy ^{160,161}.

12. APPENDIX 2: PROPERTIES OF SPHERULITES

In quiescent melts flexible linear chains crystallize into thin plate-like lamellae with the chains repeatedly folding to form a concertina type structure. These chain-folded lamellae subsequently grow to form spherulites. It has been shown that the thickness of the lamellae of polyethylene crystals, L depends on the degree of supercooling according to ^{162,163}

$$L = \frac{2\sigma_e T_m^0}{\Delta H_f \Delta T} + \delta L \quad (\text{A2.1})$$

where σ_e is the fold surface free energy that can be obtained from Lauritzen - Hoffmann theory ¹⁵⁵⁻¹⁵⁷, ΔH_f is the heat of fusion and δL is a parameter contained within kinetic theory that changes with the amount of supercooling. Equation (A2.1) suggests that the thickness of the lamellae will be inversely proportional to the amount of supercooling that occurs. This equation can be rearranged, ignoring the term δL , to give the melting temperature as a function of lamella thickness i.e.

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H_f L} \right) \quad (\text{A2.2})$$

From equation (A2.2) it is evident that the observed melting point is proportional to the thickness of each lamella which itself depends on the density of spherulites. The number of spherulites present depends on the density of nucleation sites. It therefore follows that the addition of a nucleating agent will result in the growth of a large number of small spherulites of limited thickness and hence an increase in the melting point. This effect has been shown to occur in for example in polypropylene nucleated with either glass-fibres of sodium benzoate ¹³¹.

The growth rate of spherulites, G_r can be related to the amount of supercooling that occurs ¹⁶² according to the expression

$$G_r = G_0 \exp\left(-\frac{K}{T\Delta T}\right) \quad (\text{A2.3})$$

where G_0 and K are growth rate constants. In turn G_r can be related to the melting point T_m ¹⁶³ assuming that the material is cooled at a constant rate C_r by

$$G_r = G_0 \exp \left[\frac{-K}{C_r t (T_m - C_r t)} \right]. \quad (\text{A2.4})$$

These theoretical relationships have been shown to hold for example in a study of the influence of nucleating agents on the crystallization behaviour of polyethylenes ¹³⁰.

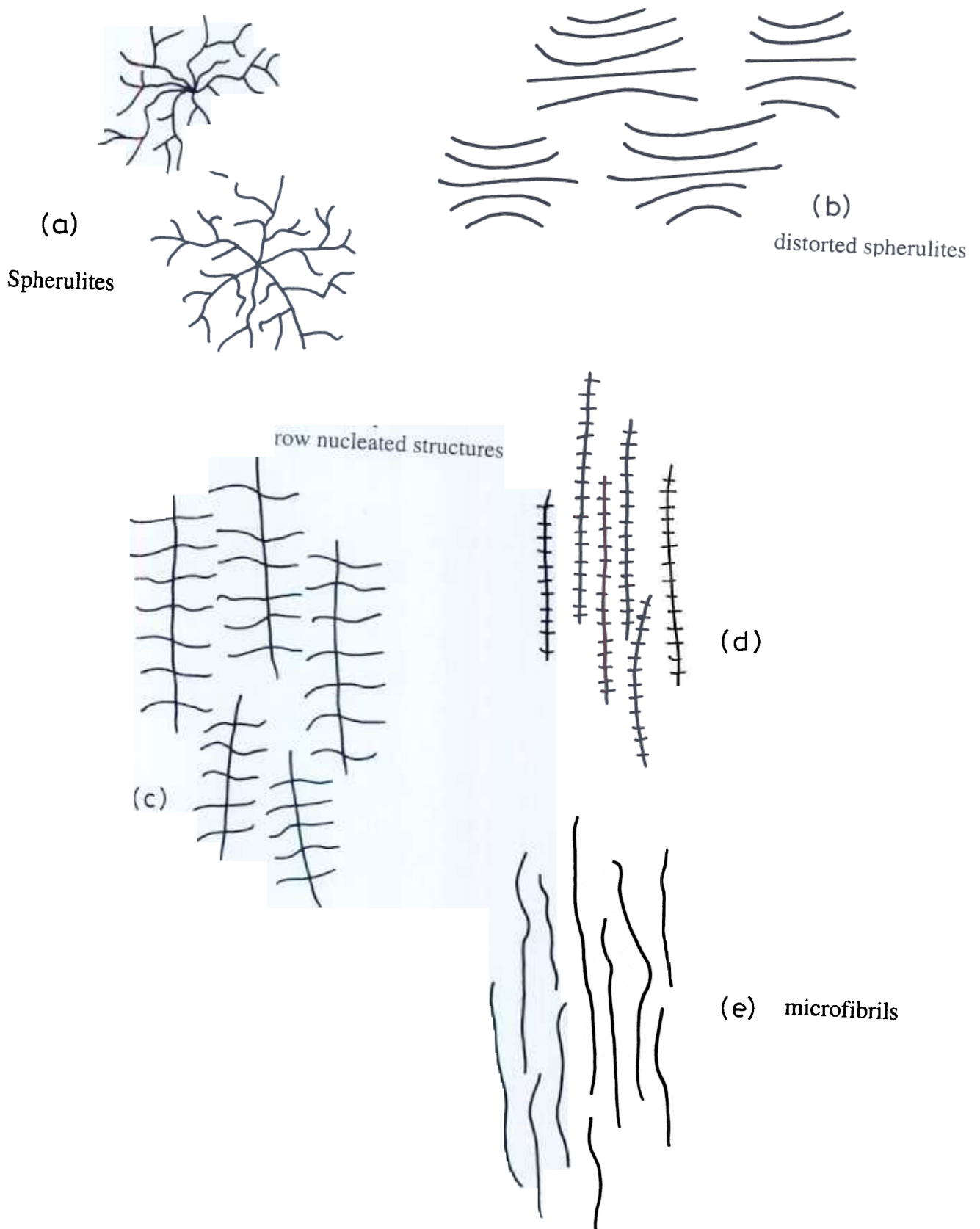


Fig 1 The influence of strain on the morphology of polymer crystals (after Hay (1604)). Schematic representations for natural rubber at strains of 0% (a), 50% (b), 100% (c), 2-300% (d) and > 300% (e).

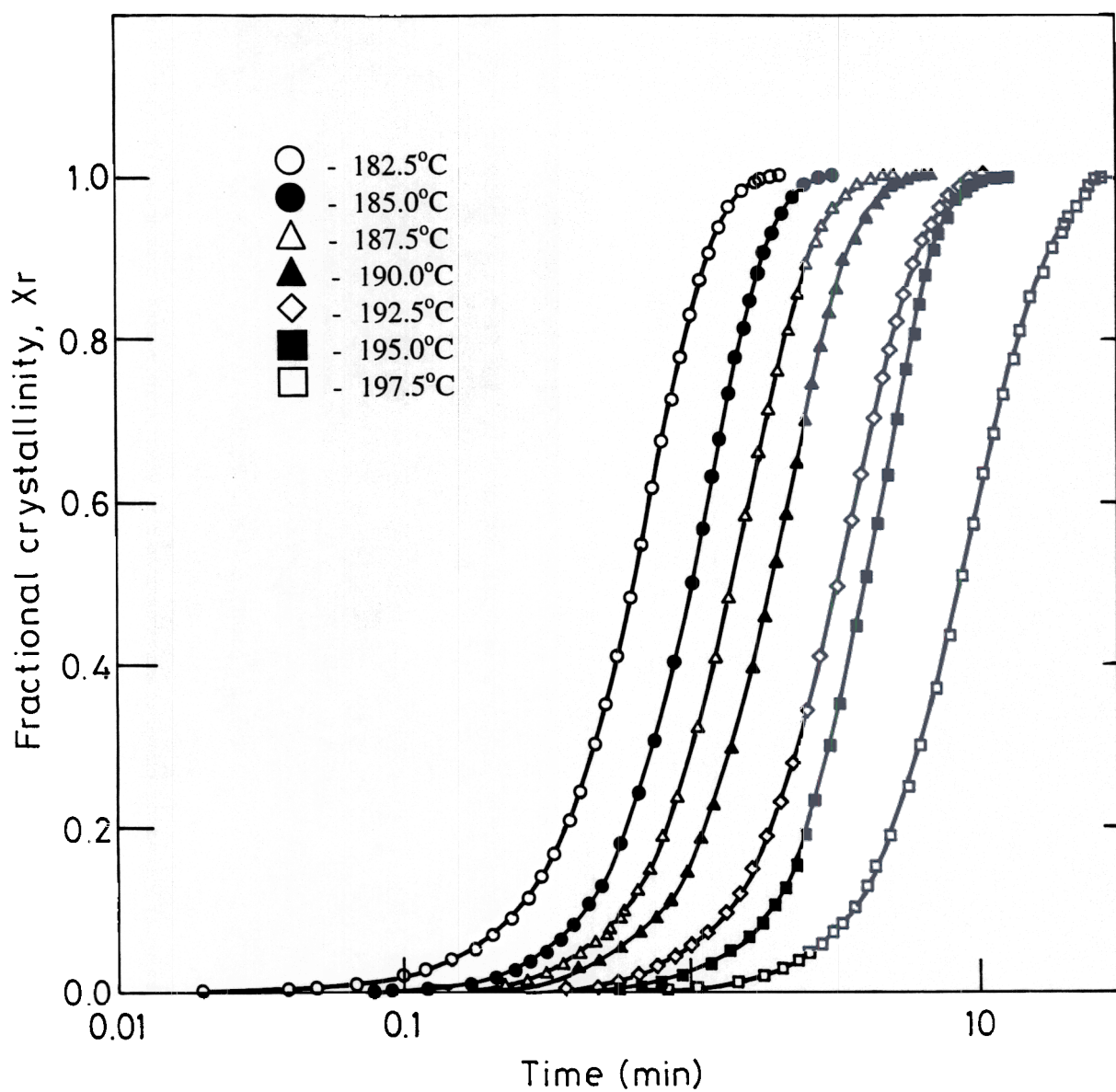


Fig 2 Characteristic sigmoidal plots of relative crystallinity as a function of log time for nylon 6 at different temperatures (redrawn from Patel and Spruiell (100))

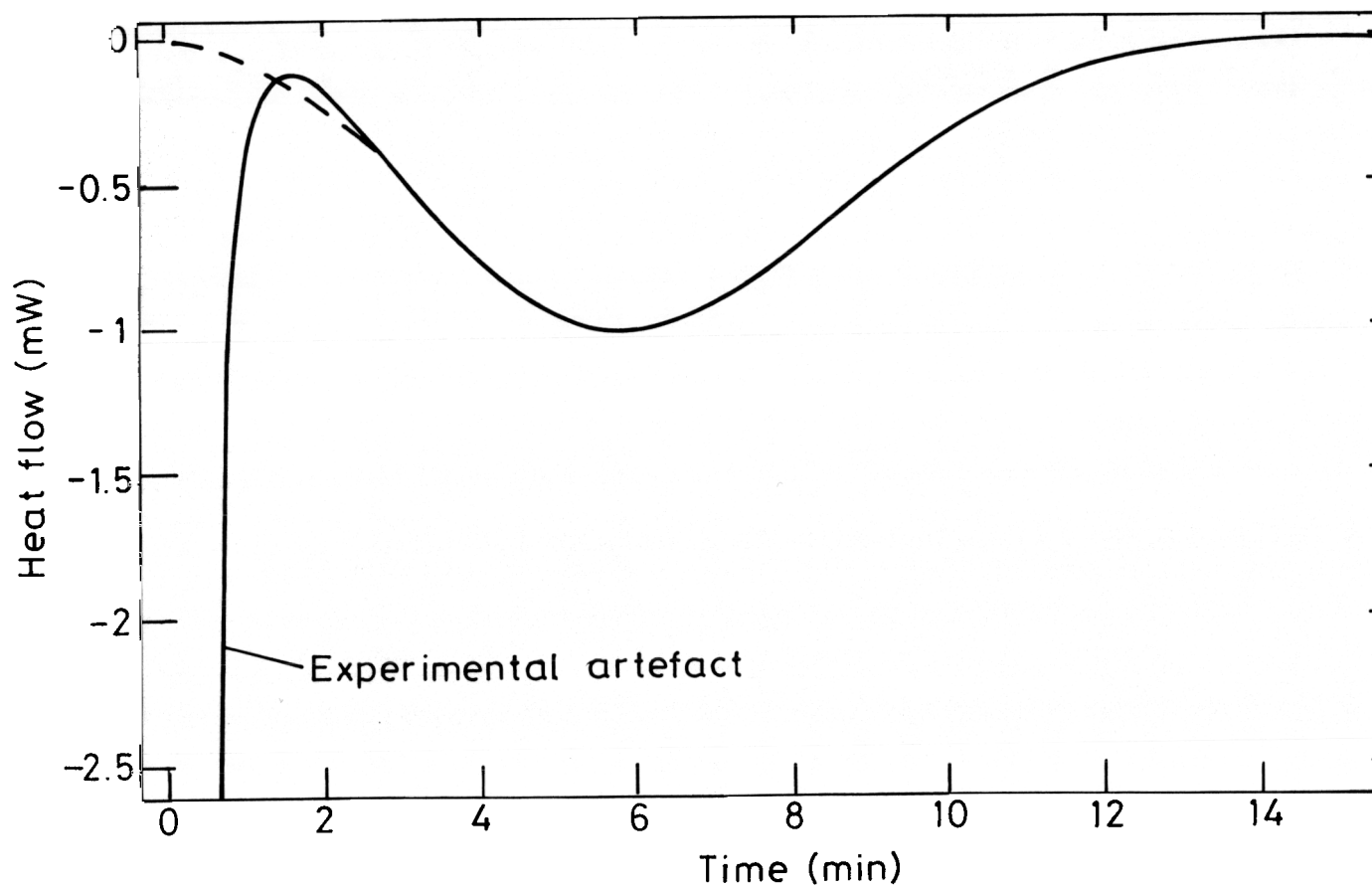


Fig 3 DSC thermogram for poly(L-lactic acid) at 110°C (after Urbanovici et al (1024)). During the early stages of crystallization, the curve overlaps with the 'machine overshoot' commonly observed after quenching a sample from some elevated temperature to the isothermal test temperature. The dotted line is an extrapolation of the crystallization curve to shorter times.

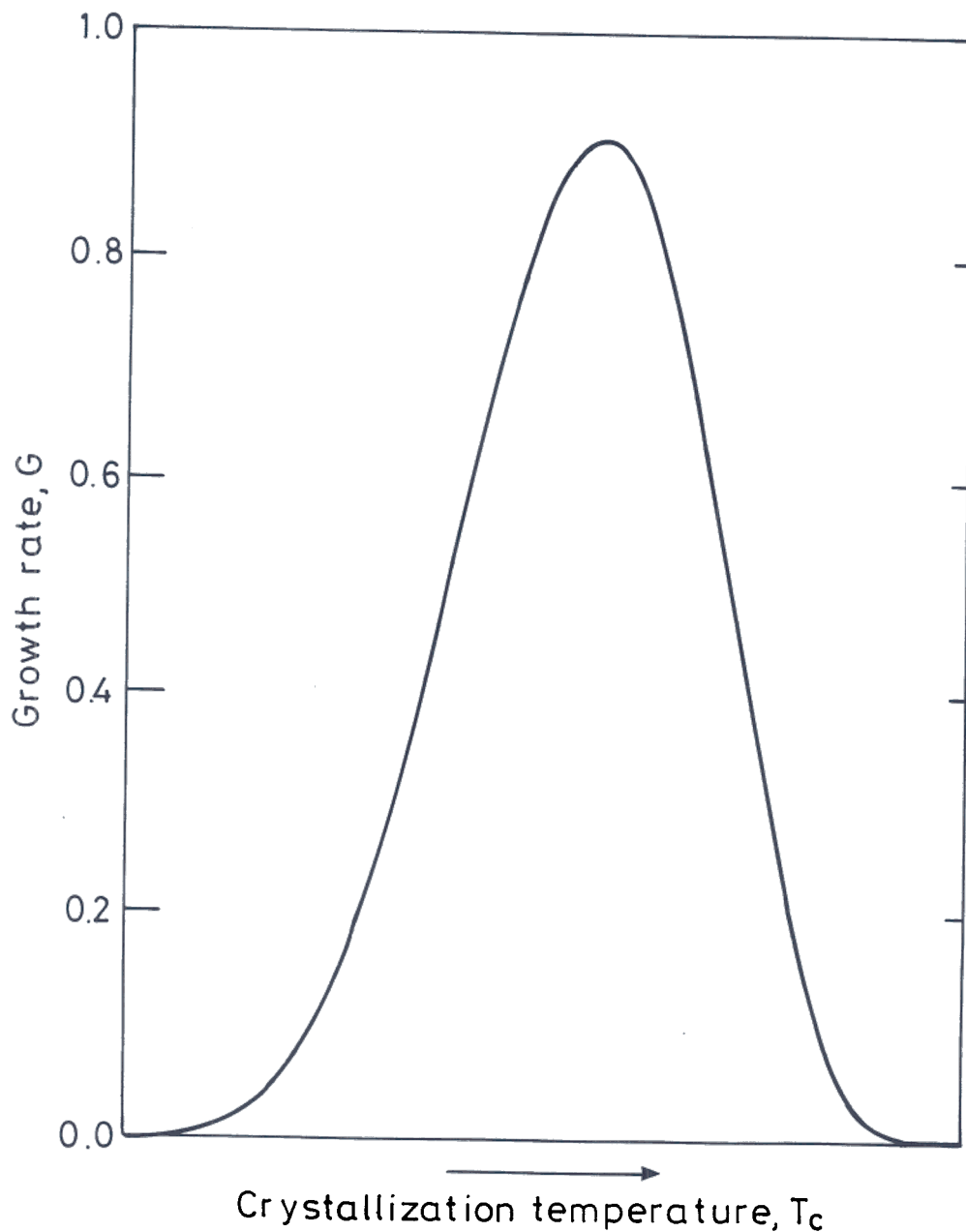


Fig 4 During isothermal experiments the rate at which crystals grow is strongly dependent on temperature. At temperatures slightly below the equilibrium melting point the driving force for crystallization is minimal thus low growth rates are observed. At lower isothermal temperatures the driving force favouring crystallization increases leading to faster growth rates. However this increasingly favourable situation is opposed by a lowering of molecular mobility as the glass transition temperature is approached which again limits the crystal growth rate.

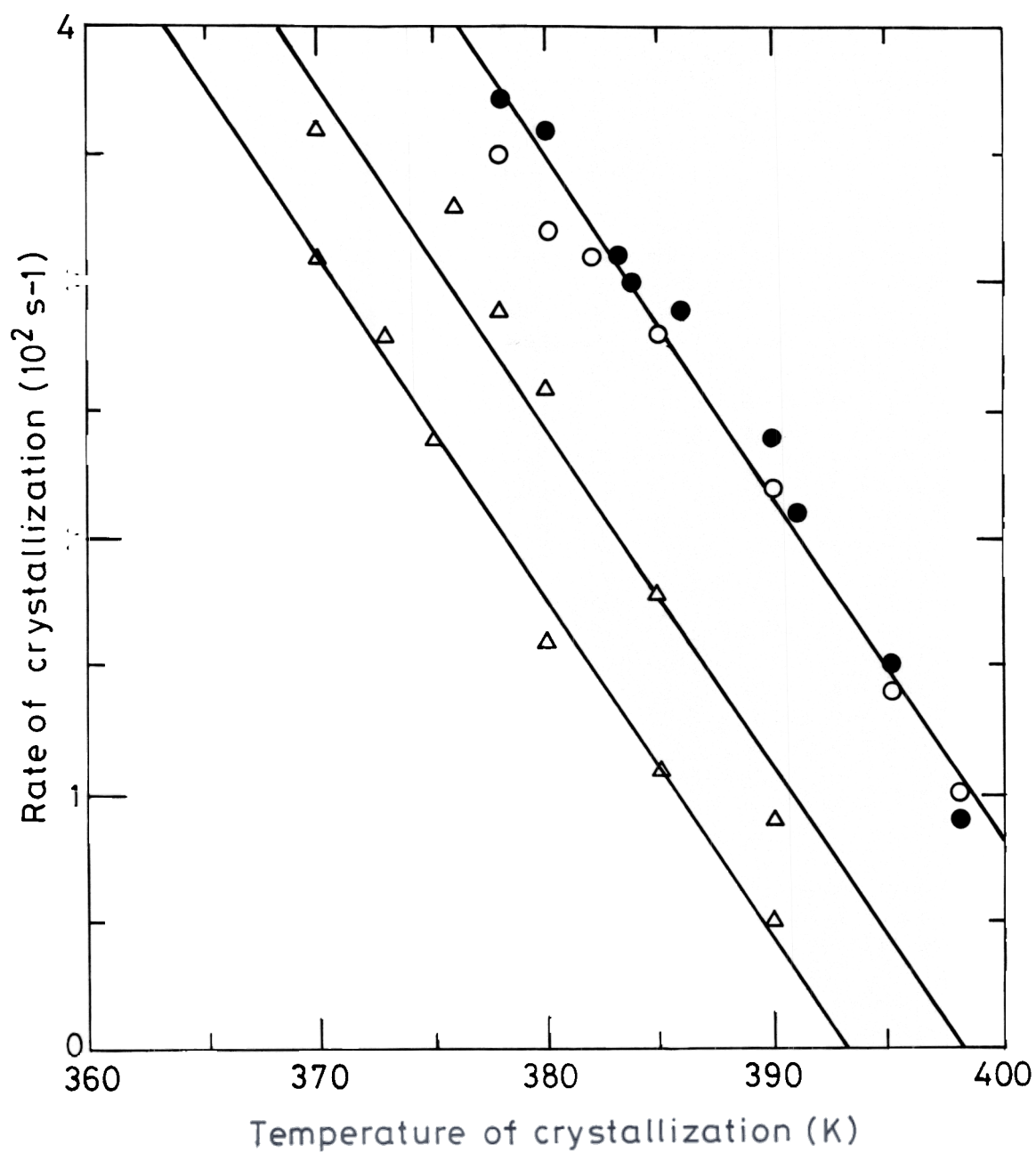


Fig 5 The influence of a nucleating agent (sodium benzoate) and short glass fibres on the rate of crystallization of polypropylene (after Iroh and Berry (1090)). The solid lines are for indication only.