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PREDICTION OF POLY(OXYMETHYLENE) NON-ISOTHERMAL CRYSTALLIZATION BEHAVIOUR FROM ISOTHERMAL DATA

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The spherulite growth, nucleation-related, K_g, parameter values obtained from isothermal data (by DSC or optical microscopy) and two other adjustable parameters (the spherulite growth rate preexponential factor and the Avrami's or Tobin's exponent, n) have been used with Nakamura's and Tobin's modified non-isothermal equations, to model the kinetics of polymer non-isothermal crystallization. Malkin's model was also tested, for comparison.

It is shown that, for polymers that crystallize on cooling almost entirely at temperatures higher than the maximum growth rate temperature, this Tobin's-like non-isothermal model accurately describes the experimental behaviour with only 2 parameters.

Keywords: DSC, non-isothermal crystallization, optical microscopy

Introduction and scope

The accurate prediction of the kinetics of non-isothermal polymer crystallization undoubtedly is a long standing scientific and technical objective, in the polymer field. Many authors have already significantly contributed to the subject [1–5] and reviewed some of the most challenging difficulties [3, 6]. A full review of previous work, however, is not intended here.

In the authors' judgement, Nakamura's work [1] stands as one of the significant and successful attempts at generalizing previous kinetic theories - mainly based on Avrami's analysis [7] - to non-isothermal conditions, by means of a straightforward integration in temperature of the basic, temperature-dependent,

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differential kinetic equation [1]. Briefly, previous Avrami's [7] or Evans' [8] formalisms are assumed to hold, with the free-growth approximation, X', now given by

$$X'(T)=\left[\int_{T_m^o}^{T} Z(T)\frac{dT}{\dot{T}}\right]^{1/n} \tag{1}$$

where $\dot{T}=dT/dt$ and $Z(T)$ is related to the usual Avrami's isothermal kinetic constant, $K(T)$, by $Z(T)=[K(T)]^{1/n}$; $Z(T)$ may thus be written [1] as

$$Z(T)=C\cdot\exp\left(-\frac{C_1 C_2}{C_2+T-T_g}\right)\cdot\exp\left(-\frac{K_g}{T\cdot\Delta Tf}\right) \tag{2}$$

The validity of Avrami's and Evans' analyses has previously been overlooked, except by Tobin [9], but is indeed highly questionable, as we concluded recently elsewhere [10–12]. So, in this work, we undertook to also reformulate the non-isothermal problem accordingly, and test the model against the experimental data.

Space being limited here, an outline of the derivation may only be provided as an Appendix to this paper. The result of a careful and much lengthier probabilistic and experimental analysis of the crystallization problem is the confirmation [11] that Tobin's equation [9] indeed describes the isothermal crystallization of polymers and metals with greater accuracy than Avrami's [7], providing the number of nuclei is infinitely large. The problem of a finite number of nuclei has also been the subject of an introductory analysis, in a generalized model [11]. The application of these same ideas to the non-isothermal case yields, instead of Nakamura's equation,

$$X(T)/[1-X(T)]=X'(T) \tag{3}$$

with $X'(T)$ given by Eq. (1).

As recently Malkin [2] proposed an entirely different model, with no less than 5 parameters, which has been providing seemingly good fits to experimental data, we also used it in this work, for comparison. In Malkin's own words, the physical significance of those parameters is problematic and non-important, an aspect that will be considered further in the Results and discussion. Details of the model are not given here, as they may be found in the original reference [2].

Procedure

As is well known, for a large number of technically important polymers, it is difficult or even impossible to measure overall crystallization or spherulite growth rates far below the melting point. Patel [3] has recently suggested a way of dealing with these cases, whereby the reciprocal crystallization half-times, $1/t_{1/2}$ (easily obtained by DSC for much wider temperature ranges than those accessible to optical microscopy), may be extrapolated and used for the lower crystallization temperatures of practical interest.

In Ref. [13], we showed that the nucleation-related K_g parameter (Eq. (2)) is the same for isothermal and non-isothermal crystallization, and may be accurately measured by DSC or optical microscopy. So, in this work, Eq. (2) has been used with the measured K_g value, to interpret the experimental non-isothermal crystallization behaviour, i.e. to predict the mass fraction transformed, X, as a function of time or temperature. For POM, whose crystallization occurs mostly above the maximum growth rate temperature, the widely accepted values of C_1 = 25 and C_2 = 30 K [13] were used, and therefore only 2 parameters had to be optimized - the pre-exponential factor C, proportional to $(1/t_{1/2})_o$, and either the Avrami's or the Tobin's exponent, n. For PEEK, however, significant crystallization occurs at lower temperatures, and the values of C_1 and C_2 also had to be optimized.

Experimental

Samples of a well characterized [13–15] POM-DELRIN 150 (T_m^o) = 198.3°C, T_g = –82 to –74°C, N-average mol.w. ≈70000 g/mol) - and of PEEK - 450G (kindly supplied by ICI), were used in this study.

The non-isothermal, controlled cooling, crystallization data were obtained by differential scanning calorimetry (dual furnace, null-balance, DSC), using a Perkin-Elmer DSC7 instrument fitted with an external block temperature control system at –90°C; cooling rates from 1 to 100 $\text{deg}\cdot\text{min}^{-1}$ were used. Prior to each run, the sample was melted and heated up to a temperature higher than the maximum melting point, without thermal degradation, and then cooled under control at the chosen rate. Duplicate runs on the same sample yielded entirely reproducible DSC traces.

For POM, isothermal DSC and optical microscopy kinetic data, for the crystallization reciprocal half-times, $1/t_{1/2}$, and spherulite growth rates, G, respectively , were previously obtained for use in this study, as described separately [13]. For PEEK, we measured by DSC [10] its K_g value ($8.217\cdot 10^4 K^2$).

Results and discussion

For POM, the non-isothermal crystallization data (at scan rates of –1, –50 and –100 $\text{deg}\cdot\text{min}^{-1}$), as well as the theoretical predictions (for X), are given in Figs 1 and 2. Figure 1 shows the extrapolated normalized spherulite growth rate data, obtained by optical microscopy and DSC ($1/t_{1/2}$)[13], and it may be seen that the entire crystallization process occurs above the maximum growth rate temperature, and so, as noted in the Procedure, an accurate prediction of the behaviour does not require exact values for C_1 and C_2 in Eq. (2).

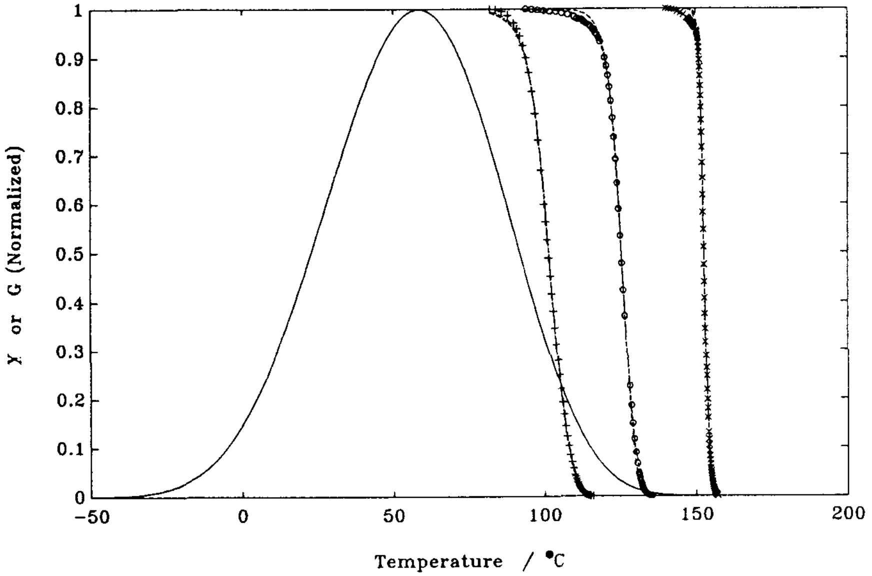

Fig. 1 Non-isothermal crystallization of POM - normalized spherulite growth rate, G (solid line) and mass fraction transformed, X, as functions of temperature: x 1 deg·min^{-1} o 50 deg·min^{-1}; + 100 deg·min^{-1}; (· – ·)Malkin's Model (5 parameters); (---) Tobin's Model (2 parameters)

In Fig. 1, the predictions of Malkin's model [2], with 5 parameters, are compared with those of the Tolbin's-like non-isothermal model presented in this work (with the DSC measured value of K_g); this model only requires 2 adjustable parameters to fit the data to a similar level of accuracy, for the same range of temperatures and crystallization extents. It is relevant to note that, while the adjustable parameters used here are physically very well defined, no reasonable and consistent interpretation may be given to the optimized Malkin's parameters [2]; in fact, not only do their values vary somewhat randomly, but also Malkin's K_g-equivalent parameter is underestimated by more than one order of magnitude, relative to the measured [13] value.

The result predicted by this new Tobin's-like non-isothermal model for the crystallization extent, X, of POM are again plotted in Fig. 2 and compared with the previous Nakamura's model [1], based on the classic Avrami's equation [7]; clearly, the fit provided by the model used here is undoubtedly superior to

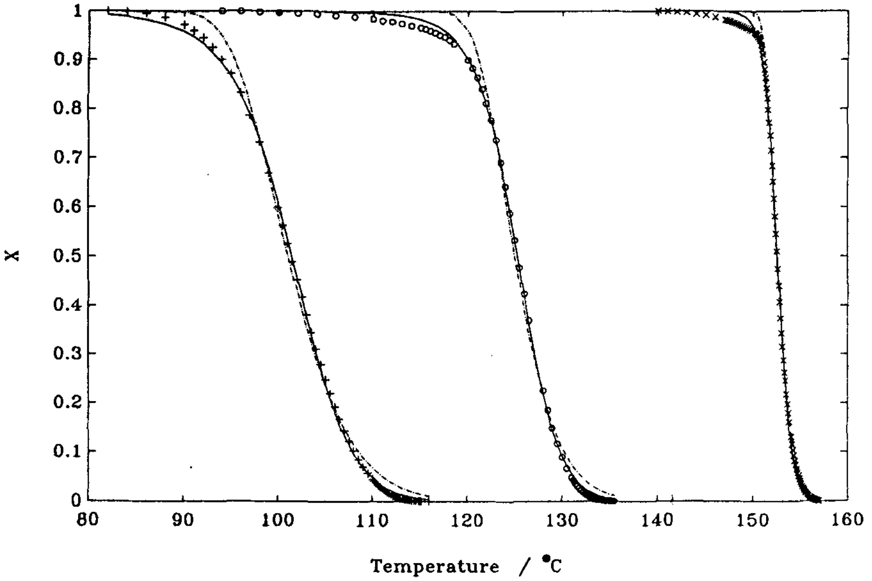

Fig. 2 Non-isothermal crystallization of POM. Comparison between Nakamura's (· — · 2 parameters) and Tobin's (—2 parameters) models

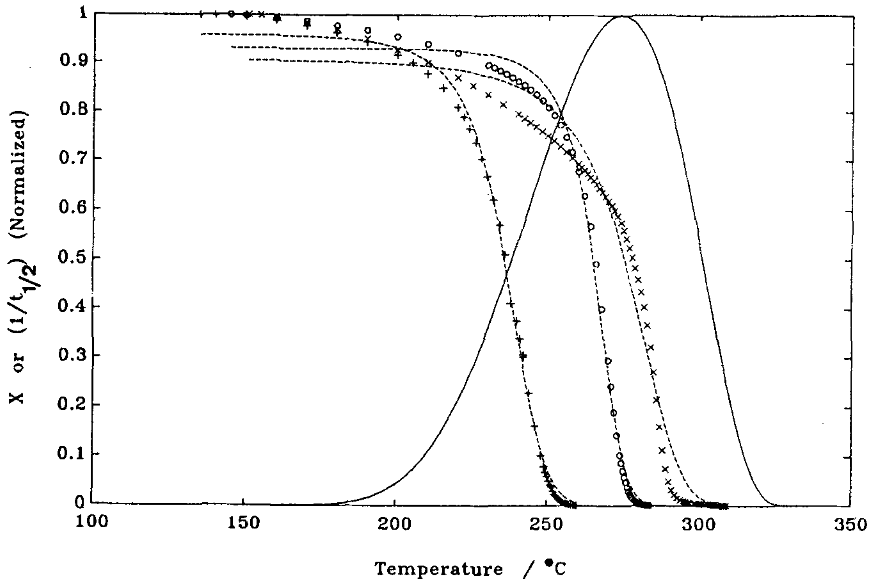

Fig. 3 Non-isothermal crystallization of PEEK - normalized reciprocal half-crystallization times, $1/t_{1/2}$ (solid line) and mass fraction transformed, X, as functions of temperature: x 5 deg·min^{-1}; o 50 deg·min^{-1}; + 100 deg·min^{-1}; (---) Tobin's Model (4 parameters)

Nakamura's, in the entire range of temperature and X values, with exactly the same number and type of parameters. For both cases, the pre-exponential factors, $(1/t_{1/2})_o$, have similar values that regularly decrease with the cooling rate, but, as may be seen in Table 1, the dimensionality parameter, n, is about one unit higher in Tobin's than in Nakamura's model. For the clearly spherulitic crystallization of POM [10–12, 16], n is expected to lie between 3 and 4, as predicted here, and not between 2 and 3. This may be additional new evidence, now for the non-isothermal case, of the physical soundness and higher accuracy of the original Tobin's model [9], despite its current neglect.

Table 1 Optimized parameter values for the Nakamura's and Tobin's Models

	Nakamura		Non-isothermal Tobin	
dT/dt / deg·min^{-1}	n	$(1/t_{1/2})_o$ / min^{-1}	n	$(1/t_{1/2})_o$ / min^{-1}
100	2.95	$1.67 \cdot 10^7$	4.04	1.86·107
50	2.26	$1.08 \cdot 10^8$	3.07	$1.23 \cdot 10^8$
20	2.06	$5.80 \cdot 10^8$	2.83	$6.65 \cdot 10^8$
10	2.17	$9.30 \cdot 10^8$	2.82	$1.05 \cdot 10^9$
5	2.23	$1.67 \cdot 10^9$	2.90	$1.88 \cdot 10^9$
1	2.49	$1.58 \cdot 10^9$	3.56	$1.79 \cdot 10^9$

Finally, Fig. 3 shows results obtained with PEEK, a polymer that, certainly due to its rigidity, undergoes substantial crystallization below the maximum growth rate temperature, as assessed from the $1/t_{1/2}$ DSC data [10]. It may be seen that the quality of the theoretical predictions is now much poorer, even when C_1 and C_2 are also adjusted (4 parameters). Possible reasons for the behaviour of this relatively new polymer may be some inadequacy of the assumed temperature dependence(Eq. (2)) of the diffusion-related activation energy [13], or even the occurrence of a multistage crystallization process. This will be looked at in our continuing work, by means of additional DSC $1/t_{1/2}$ measurements, by temperature jump experiments from below T_g.

Conclusions

1. It is possible to predict, with reasonable accuracy, the course of the non-isothermal crystallization of polymers, from purely isothermal data;

2. For polymers whose crystallization on cooling develops mainly at temperatures higher than the maximum growth rate temperature, the non-isothermal crystallization is well described by a Tobin's-like equation (having only two parameters), with the K_g value obtained by isothermal DSC (or OM) data; the

agreement with the experimental data is better than with the previous Nakamura's model, and equivalent to Malkin's 5 parameters model;

3. For other polymers, like PEEK, a good fit may perhaps be obtained only with a better knowledge of (T_{max}, G_{max}), and of the diffusional effects that operate at temperatures near T_g.

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Appendix: Tobin's model (A new derivation)

X = mass fraction transformed; t = time;
X' = free growth solution (no interaction with neighbouring spherulites);
The arrivals of crystalline growth fronts to an arbitrary point within the melt are Poisson events (U. R. Evans);
The average number of arrivals cannot be assumed equal to $X'(t)$, because it must not tend to infinity at long times;

$P(\cdots)$ = probability; $P(\cdots|\cdots)$ - conditional probability.

$$P(\text{Zero Arrivals}, t+\mathrm{d}t)=P(\text{Zero Arrivals}, t)\cdot P(\text{Zero Arrivals}, \mathrm{d}t \mid \text{Zero Arrivals}, t)$$

Making $Y=1-X(t)$ = untransformed fraction

$$Y(t+\mathrm{d}t)=Y(t)\cdot[1-P(1\ \text{Arrival}, \mathrm{d}t \mid \text{Zero Arrivals}, t)]$$

$$Y(t+\mathrm{d}t)=Y(t)\cdot[1-Y(t)\cdot(\mathrm{d}X'/\mathrm{d}t)\,\mathrm{d}t]$$

$$-\mathrm{d}Y/Y^2=\mathrm{d}X' \text{ and } (1-Y)/Y=X'=Kt^n$$

$$X/(1-X)=Kt^n \text{ or } X=Kt^n/(1+Kt^n)$$

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Zusammenfassung — Zur Modellierung der Reaktionskinetik der nichtisothermen Polymerkristallisation wurden unter Anwendung der modifizierten nichtisothermen Gleichung von Nakamura und Tobin der Sphärolithwachstumsparameter K_g (ermittelt durch DSC oder optischer Mikroskopie aus den isothermen Daten) und zwei weitere Stellparameter (der präexponentielle Faktor der Sphärolithwachstumsgeschwindigkeit und der Avrami- oder Tobin-Exponent *n*) verwendet. Zum Vergleich wurde auch das Modell von Malkin getestet. Es wurde gezeigt, daß für Polymere, die beim Abkühlen fast vollständig kristallisieren, oberhalb der Temperatur für die maximale Wachstumsgeschwindigkeit das nichtisotherme Tobin-sche Modell das experimentelle Verhalten mit nur 2 Parametern exakt beschreibt.