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Crystallization kinetics of iPP. Model and experiments

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Summary

The model proposed by Ziabicki [1] [2] for non-isothermal crystallization kinetics was adopted in this work, to describe the crystallization kinetics of a commercial iPP under a very wide range of conditions (i.e. isothermal, slow-cooling rate and high-cooling rate (up to 200 °C/s) from the melt). A modification of the model was required in order to achieve a good agreement between model predictions and the whole set of experimental data.

Introduction

Crystallization kinetics of polymers has been widely investigated by a large amount of theoretical and experimental works.

Early models (Kolmogoroff, [3]; Avrami, [4]; Evans, [5]) concerned with systems kept under constant temperature thus ignoring the dependence of crystallization rate on temperature history. Following papers (Nakamura *et al.*, [6]; Ozawa, [7]) accounted for temperature changes during crystallization, under the so called isokinetic hypothesis, i.e. proportionality between crystal nucleation and growth rate. Under isokinetic assumption model parameters can be identified by simple isothermal and slow cooling experiments, easily carried out by means of differential scanning calorimetry (DSC).

The role of cooling rate in the Nakamura model, its modifications and other model that neglect athermal effects is mainly that of normalizing the kinetic constant which is not directly function of cooling rate.

In a recent series of papers, Ziabicki [1] [2] proposed a model of polymer crystallization kinetics accounting for both transient and athermal effects. Moreover, researchers of the University of Palermo (Brucato *et al.*, [8]; Piccarolo *et al.*, [9]) developed and adopted an experimental procedure to investigate the crystallization of polymers under fast cooling.

In this work crystallization kinetics of iPP was investigated, by both a traditional set of experiments (DSC) and fast cooling measurements. Results of these experiments are compared with predictions of the model proposed by Ziabicki.

Experimental

The resin adopted for the experiments performed in this work is a commercial iPP

Isothermal and slow cooling-rate tests (up to 1°C/s) were performed by a DSC apparatus (Perkin Elmer DSC7). Thin polymer samples held between two copper plates were quenched by water sprays in the apparatus schematically shown in Figure 1, and temperature history during quenching were measured by a suitable thermocouple connected to a data acquisition system. Cooling rates up to about 200°C/s were obtained. Density, measured in a density gradient column, and from FT-IR absorbance spectra, obtained with a MIDAC 2000 spectrometer, was determined on final products of all cooling experiments (DSC and quenches). Crystallinity index was calculated from density and FT-IR spectra on the basis of absorbance at some characteristic peaks (ν=841 cm^{-1} for crystalline phase, ν=973 cm^{-1} for amorphous phase) [10].

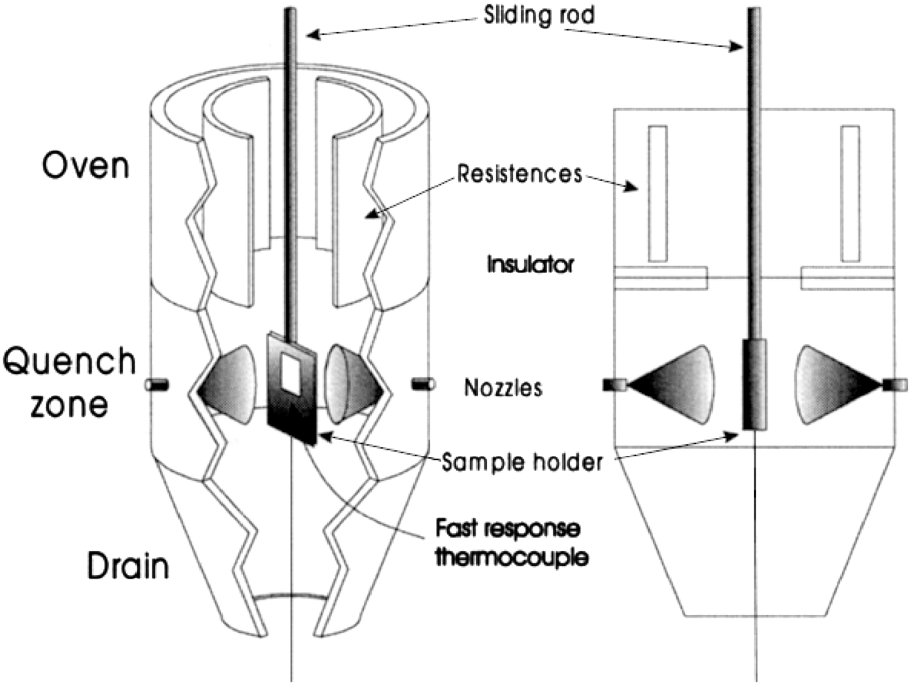

Figure 1. Device for performing quench tests

The Model

The traditional Kolmogoroff-Avrami-Evans equation is the basis for the description of *time-evolution* of crystallinity, i.e. the crystallization kinetics. Denoting the volume fraction of the crystallized material by χ_c, the function $P(t)$ defined by

$$\chi_c(t) = \frac{X_c(t)}{X_{eq}} = 1 - \exp\{-[P(t)]^n\} \quad (1)$$

is often adopted as a non-linear description of crystallinity; in addition its time-derivative $K(t)$

$$K(T) = \frac{d}{dt} P(t) \quad (2)$$

is a measure of crystallization rate and is usually identified as crystallization kinetics constant. The model, first proposed by Ziabicki [1] [2] for crystallization kinetics is here simplified as follows:

$$K(T) = K_{th}(T)\left(1+\dot{T}Z(T)\right)^{\frac{1}{n}} \tag{3}$$

Where $K_{th}(T)$ identifies the values of the crystallization kinetics constant in the limit of low values of cooling rate and $Z(T)$ is a function (athermal function) which accounts for the effect of cooling rate on crystallization kinetics constant $K(T)$. Assuming the hypothesis of heterogeneous nucleation, the dependence of the material functions K_{th} and Z (athermal function) upon temperature, was taken as [2] (κ_1, κ_2, E_a are material parameters, T_m^0 is equilibrium crystallization temperature and R is the universal gas constant):

$$K_{th} = \kappa_1 \frac{T\left(T_m^0 - T\right)}{\left(T_m^0\right)^2} \exp\left[-\frac{E_a}{RT}\right] \exp\left[-\kappa_2 \frac{\left(T_m^0\right)^2}{T\left(T_m^0 - T\right)}\right] \tag{4}$$

$$Z = -C_{ath} \frac{\left(T_m^0\right)^5}{T\left(T_m^0 - T\right)^5} \exp\left[\frac{E_a}{RT}\right] \tag{5}$$

In Ziabicki's theoretical treatment, the athermal coefficient C_{ath} was assumed being a constant parameter. Experimental results will allow to check this assumption for the iPP resin used in this work.

Results and discussion

Results of isothermal calorimetric tests are summarized in Figure 2. Classical Avrami analysis allows to calculate values of Avrami's index (n) and rate-constant (K). Time evolution of crystallinity during all isothermal tests were sufficiently described taking n=3, which can be explained by heterogeneous nucleation followed by three-dimensional crystal growth. Values of K, which under isothermal conditions is K_{th}, are reported in Figure 3. Results of DSC cooling procedures are reported in Figure 4. Maximum crystallization rate temperatures, i.e. temperatures corresponding to a maxima in crystallization rate, calculated in agreement with [11], very close to maxima in DSC peaks, are reported in Figure 5 versus cooling rates. At last, crystallinities measured by density and FT-IR, of samples solidified during cooling experiments (DSC and quenches) are reported in Figure 6.

Once the value of n has been determined as 3, only four parameters are left, namely κ_1, κ_2, E_a, and C_{ath}. Three optimisation procedures were carried out. Only the parameters κ_1, κ_2 and E_a were first optimized of isothermal DSC tests only. Comparison between experimental results and model predictions (identified as optimization 1) are shown in Figures 3, 5 and 6. In particular, predictions of kinetics constant as function of temperature and of maximum crystallization rate temperature

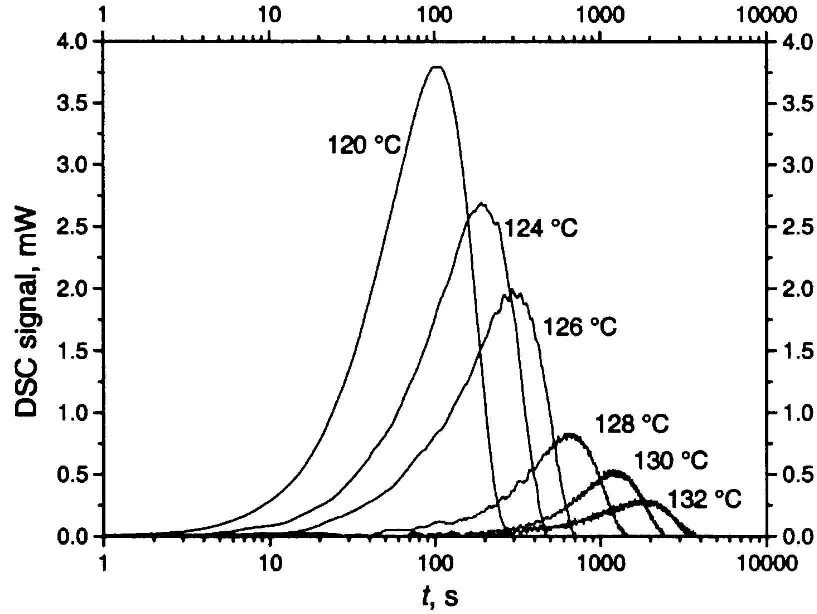

Figure 2. DSC esothermal signal during isothermal tests

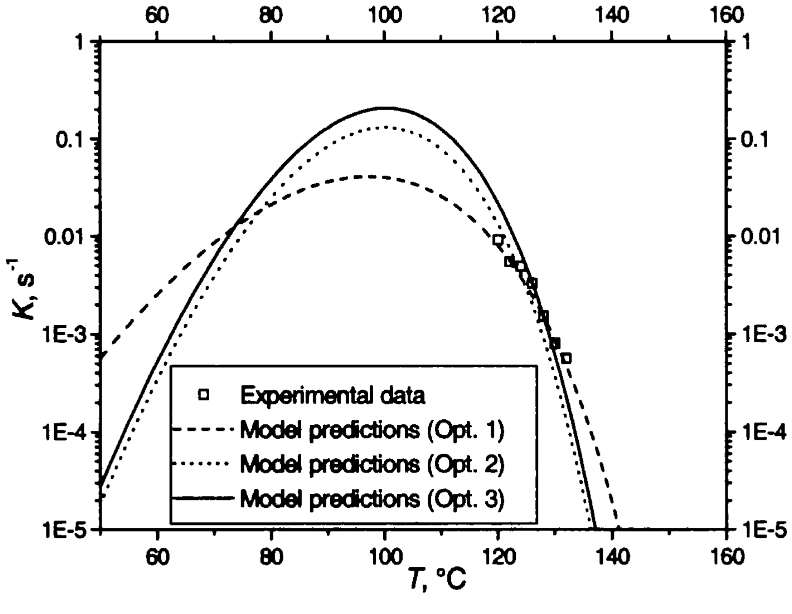

Figure 3. Values of isothermal crystallization rate, *K*

as a function of cooling rate, reported in Figures. 3 and 5, respectively, leads to a good description of experimental results. Vice versa, the experimental behaviour of final crystallinity as a function cooling rate is not reproduced by model predictions, especially at high cooling rates (Figure 6).

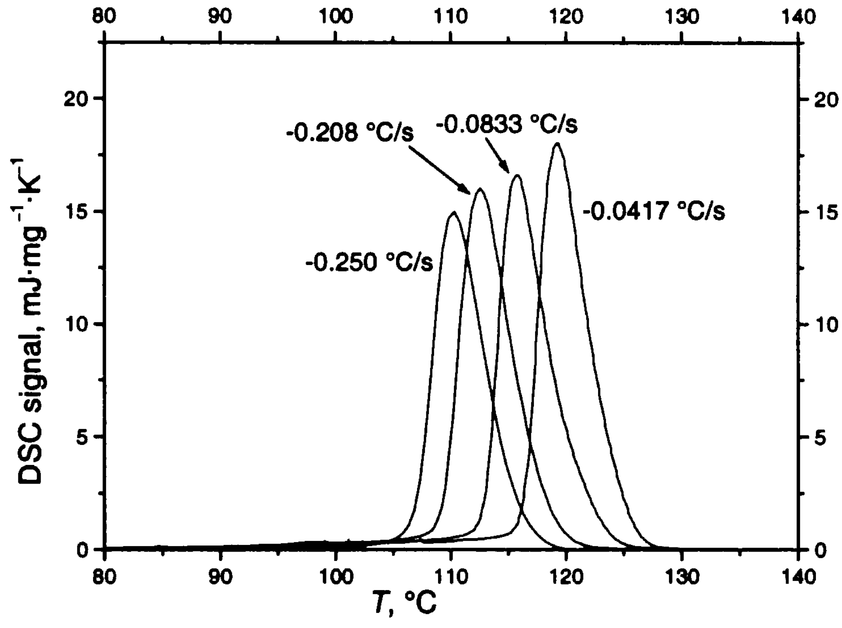

Figure 4. Normalized DSC signal during cooling tests

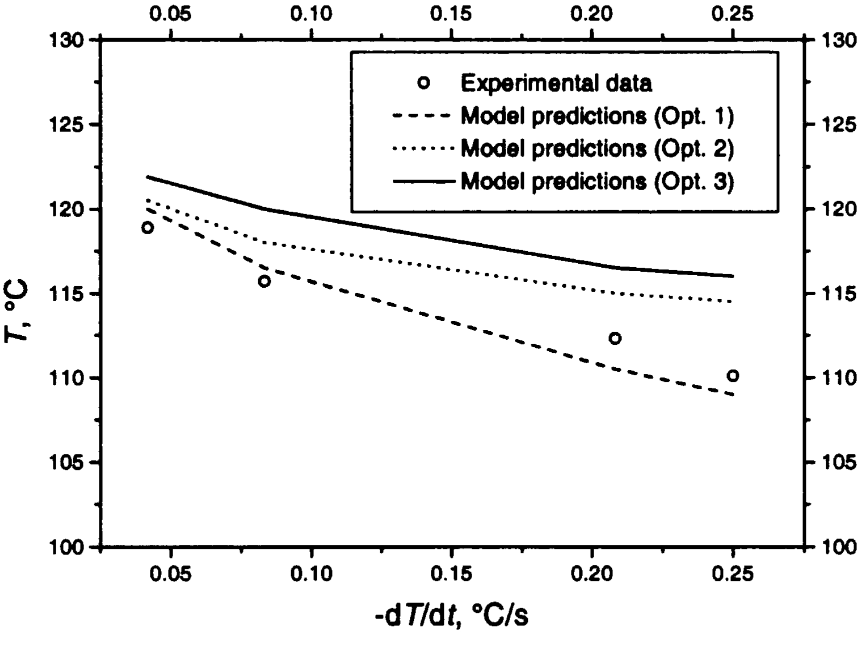

Figure 5. Maximum rate temperature in DSC tests and model predictions

The four parameters κ_1, κ_2, E_a, and C_{ath} were then optimized over the whole set of data (calorimetric and quenches). Corresponding model prediction also reported in Figures 3, 5 and 6 (identified as optimization 2), was again poor, especially the prediction of final crystallinity of samples solidified at high cooling rates.

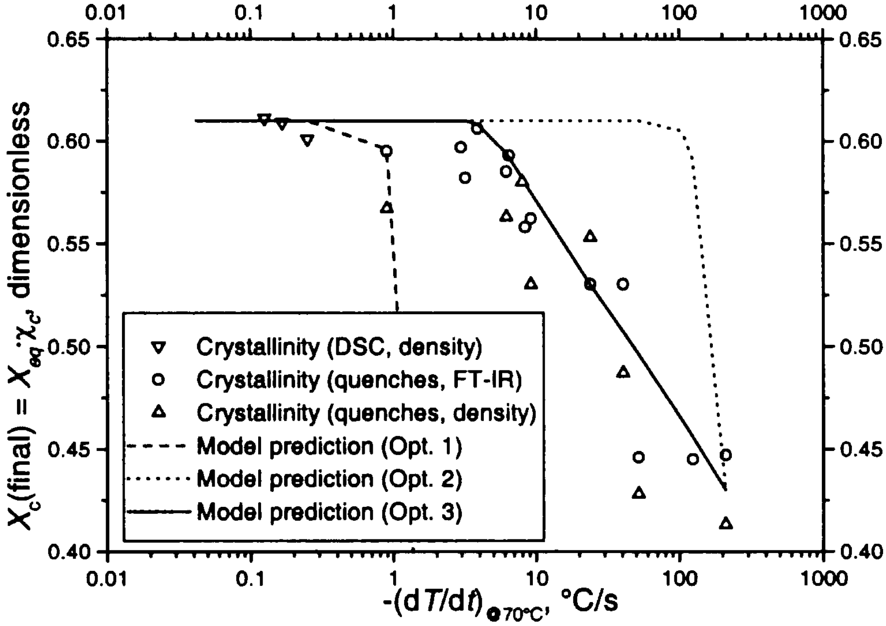

Figure 6. Crystallinity: experimental data and model predictions

Obviously, a much better description of the whole set of data was achieved taking C_{ath} function of cooling history, and in particular of the cooling rate measured in the crystallization temperature interval (which for iPP was found to be 70°C, Piccarolo *et al.*, [12]). The values of C_{ath} which allowed best fitting of each cooling experiment (holding constant the values of κ_1, κ_2, E_a predetermined through the isothermal tests) are shown in Figure 7 as function of cooling rate at 70°C. These results are well aligned along a straight line suggesting to take C_{ath} proportional to a power of $\dot{T}$ (A_{ath} and B_{ath} are material parameters):

$$C_{ath} = B_{ath}\left|\dot{T}\right|^{A_{ath}} \tag{6}$$

In the crystallization model C_{ath} was then taken as a function of $\dot{T}$ according to eq. (6).

The whole set of data was reconsidered taking κ_1, κ_2, E_a, B_{ath} and A_{ath} as free fitting parameters. The result of the regression, shown in Figures 3, 5 and 6 (identified as optimization 3), gives a satisfactory description over the whole range of crystallization conditions, which is very wide. The full set of parameters identified by optimisation 3 is reported in table 1.

X_{eq}	0.61	dimensionless	κ_1	$2.778\cdot10^{69}$	1/s
n	3	dimensionless	κ_2	5.871	dimensionless
T_m^0	463.15	K	A_{ath}	1.7721	s
E_a/R	45570	K	B_{ath}	$3.448\cdot10^{-57}$	dimensionless

Table 1. Values of fitting parameters (Optimization 3)

Conclusions

A set of parameters which, adopted in the model proposed by Ziabicki for crystallization kinetics, assured a good description of isothermal and slow cooling rate experimental results did not give a satisfactory description of final crystallinities of samples solidified under very high cooling rates.

A poor description of the experimental results was attained even after optimization of parameters of the Ziabicki model over the whole set of data.

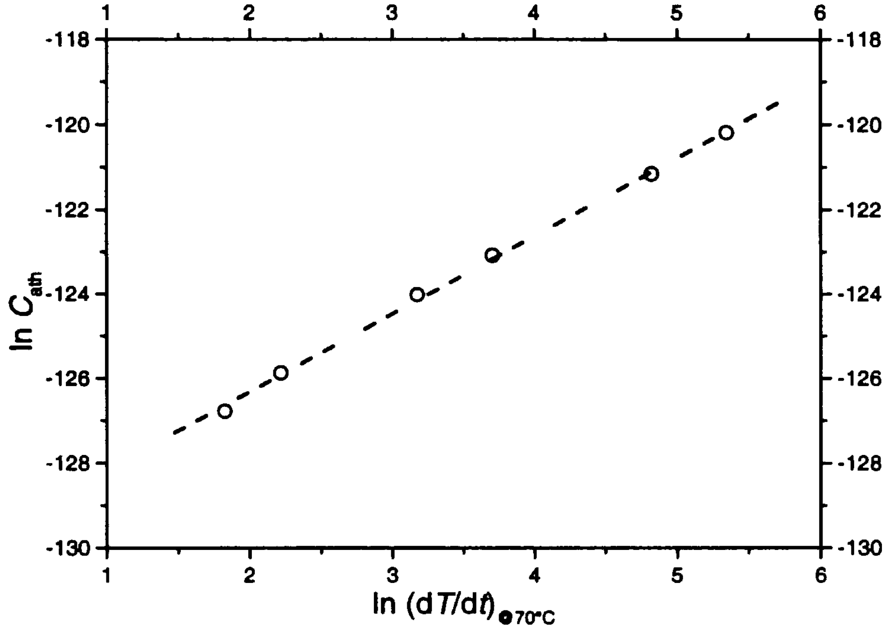

Figure 7. Athermal coefficient C_{ath} vs. characteristic cooling rate

A good description of the data was achieved only taking the athermal constant, C_{ath} function of cooling rate. Such a modification of the Ziabicki model may be required in the simulation of processing operations which involve low and very high cooling rates.

References

1. Ziabicki, A.; *Coll. Polym. Sci.*, **274**, 209 (1996a)
2. Ziabicki, A.; *Coll. Polym. Sci.*, **274**, 705 (1996b)
3. Kolmogoroff, A. N.; *Isvest. Akad. Nauk. SSSR Ser. Math.*, **1**, 335, (1937)
4. Avrami, M.; *J. Chem. Phys.*, **7**, 1103, (1939) and *J. Chem. Phys.*, **8**, 212, (1940) and *J. Chem. Phys.*, **9**, 177, (1941)
5. Evans, U. R.; *Trans. Faraday Soc.*, **41**, 365, (1945)
6. Nakamura, K.; Watanabe, T.; Katayama, K.; Amano, T.; *J. Appl. Polym. Sci.*, **16**, 107, (1972) and Nakamura, K.; Amano, T.; Watanabe, M.; *J. Appl. Polym. Sci.*, **17**, 1031, (1973)
7. Ozawa, T.; *Polymer*, **12**, 150, (1971)
8. Brucato, V.; Crippa, G.; Piccarolo, S.; Titomanlio, G.; *Polym. Eng. Sci.*, **31**, 1411, (1991)

9. Piccarolo, S.; Saiu, M.; Bucato, V.; Titomanlio, G.; *J. Appl. Polym. Sci.*, **46**, 625, (1992)
10. Lamberti, G.; Brucato, V.; Titomanlio, G.; *Proceedings of CHISA 2000*, 14th International Congress of Chemical and Process Engineering, 27 - 31 August 2000, Praha, Czech Republic
11. Eder, G.; Janeschitz-Kriegl, H.; in *Processing of Polymers, Materials Science and Technology*, Vol. 18, Meijer, H.E.H. (Ed.), John Wiley & Sons, (1997)
12. Piccarolo, S.; Alessi, S.; Brucato, V.; Titomanlio, G.; in *Crystallization of Polymers*, Ed. M. Dosière, NATO ASI Series, Kluwer Academic Publisher, 475, (1993)