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A new kinetic model for polymer crystallization derived by calorimetric analysis [1]

J.M. Kenny [a,*], A. Maffezzoli [b] and L. Nicolais [c]

[a] *Istituto Chimico, Facoltà di Ingegneria Università di Catania, Vle. A. Doria 6, 95125 Catania, Italy*
[b] *Dipartimento di Scienza dei Materiali, Univeristà di Lecce, Via Arnesano, 73100 Lecce, Italy*
[c] *Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli, P. Tecchio 80125 Naples, Italy*

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Abstract

Calorimetric results obtained by differential scanning calorimetry (DSC) have been used to develop a macrokinetic model for the crystallization behavior of semi-crystalline polymeric materials. The model, taking into account the effects of nucleation and crystal growth, is able to describe the kinetics of crystallization in isothermal and non-isothermal conditions, including cold crystallization and melt crystallization. Experimental data obtained in a wide range of thermal conditions for pure PPS film and for PPS matrix composite compare well with theoretical results. Time–temperature–transformation plots constructed from the model are presented, providing a fundamental tool for understanding the crystallization behavior of semi-crystalline matrices and for determining the most appropriate processing conditions.

INTRODUCTION

Calorimetry may be considered as one of the most interesting techniques for macrokinetic analysis of polymer crystallization. The study of the crystallization kinetics of polymers and polymer matrices for composites as a function of the processing conditions, from a macrokinetic point of view, is very important for analysis and design of processing operations. In fact, during fabrication, the polymeric material must be heated above its melting temperature under controlled conditions in order to obtain a viscous fluid that can be shaped under pressure according to the correct technological process. Then, the formed parts are cooled to room temperature, leading

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* Corresponding author.

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to the formation of the crystalline structure responsible for the physical properties of the final products. Normal processing conditions may involve cooling rates in the order of several hundred degrees centigrade per minute, leading to amorphous regions characterized by lower mechanical properties and poor thermal and environmental resistances [1–5].

In the macrokinetic approach, the dependence of the degree of crystallization on time and temperature must be defined in order to model and optimize the final crystalline structure of the polymer. Although the kinetics of polymer crystallization has been studied for a long time [6, 7], many experimental and theoretical questions are still unsolved because of the complexity of the nucleation and growth phenomena of macromolecular crystals. In particular, the melting history of a polymer can modify the crystallization kinetics, acting on the nucleation process or altering the polymer structure due to to branching, partial crosslinking or degradation phenomena [8, 9]. Moreover, as a consequence of the experimental restrictions of the currently available techniques, the crystallization kinetics can normally only be analyzed in a narrow temperature interval and under low cooling rates. In the case of composite materials, the effect of the fibers must also be considered. Fibres may act on crystallization as nucleating agents, modifying the crystal morphology, and reducing the maximum degree of crystallinity as a consequence of the steric hindrance offered to crystal growth [8–11].

In this work, a simple macrokinetic model for the crystallization of pure polymers and composite matrices, that can be used for process modelling, is proposed. The theoretical model allows the description of the crystallization behavior of thermoplastic polymers during processing under normal thermal conditions, including cold crystallization and melt crystallication, and quenching. The results of the calorimetric characterization of pure poly(phenylene sulfide) (PPS) film and of PPS matrix/carbon fiber composite, performed under a wide range of thermal conditions, are used to develope and test the model.

EXPERIMENTAL

Thermal analysis experiments were performed on two PPS-based materials provided by Phillips Petroleum Co.: PPS neat film and PPS matrix prepreg Ryton AC-66, reinforced with 60% of carbon fibers.

The development of crystallinity was monitored on samples containing approx. 15 mg of polymer (30–40 mg of prepreg) by calorimetric analysis, using a Mettler DSC 30 differential scanning calorimeter (DSC), operating from −50 to +350°C in nitrogen atmosphere.

PPS materials have a T_g of 85°C, and a $T_m^{\ominus}$ value of 303°C is assumed from literature data [12]. Preliminary DSC analysis of the as-received materials confirmed that, from the similarity of the crystallization and melting peak areas, they can be considered amorphous, as previously reported for the same materials [13]. In isothermal melt crystallization experiments, the samples were molten for 10 min at 320°C, and then rapidly cooled at the constant test temperature. The same melting history was used for non-isothermal crystallization experiments. Cold crystallization tests were performed by heating the originally amorphous material above T_g. Although these materials show a slow crystallization process compared to other polymers (such as polyethylene or polypropylene), the temperature range that can be explored is limited by the strong dependence of the crystallization rates on the test temperature, and also information provided by non-isothermal experiments must be considered for full model verification. For these reasons only a range of less than 20°C may be explored in cold crystallization and melt crystallization experiments for both materials. Suitable experimental data were obtained between 120 and 135°C (cold crystallization) and between 230 and 245°C (melt crystallization). Accurate data in non-isothermal experiments were obtained at cooling rates below 30°C min^{-1}.

RESULTS AND DISCUSSION

Crystal nucleation

Isothermal and non-isothermal DSC tests were performed on both materials studied, at different temperatures and cooling rates respectively. An isothermal thermogram and a non-isothermal thermogram obtained on the PPS film are shown in Figs 1 and 2, respectively. While the delay in the DSC signal for the non-isothermal thermogram (Fig. 2) could be attributed to a thermal effect on the kinetics of crystal growth, the delay of the DSC

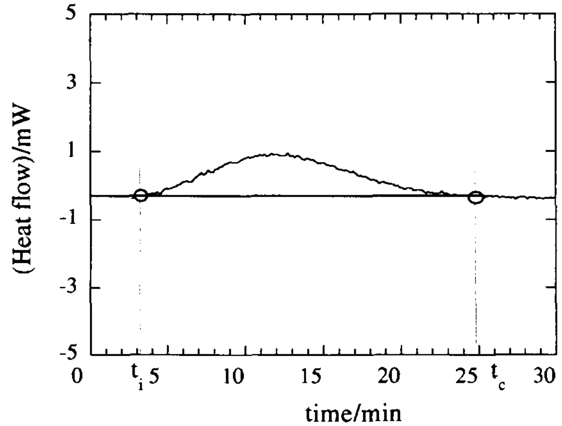

Fig. 1. Isothermal DSC thermogram obtained during melt crystallization at 240°C; t_i and t_c represent the induction and the crystallization time, respectively.

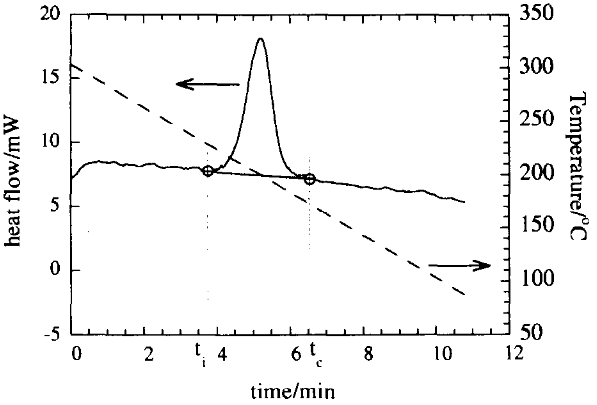

Fig. 2. DSC thermogram showing the crystallization obtained during cooling from the melt at $-20°\mathrm{C\,min}^{-1}$; t_i and t_c represents the induction and the crystallization time, respectively, computing the time starting from the melting temperature $T_m^{\ominus} = 303°\mathrm{C}$.

signal for the test performed under isothermal conditions surely represents an induction time, a relevant parameter from a processing point of view, associated with crystal nucleation. Nucleation is heterogeneous in nature in most polymers used for commercial applications because nucleation agents are usually added in order to accelerate the overall crystallization process [6]. Moreover, in polymer composites, fiber surfaces can act as nucleating agents, contributing significantly to heterogeneous nucleation. The effect of carbon fibres on the induction time during crystallization of PPS matrix composites has already been reported [13]. Heterogeneous nucleation is a thermally activated phenomenon that can be characterized by measuring the induction time as a function of the test temperature in isothermal DSC experiments [6]. However, the effect of the induction times is more complex in non-isothermal crystallization experiments where a time–temperature superposition is verified; in any case, it plays a fundamental role in determining the onset time for the crystal growth. Crystallization models that neglect the effects of nucleation lead to unsatisfactory results [14].

In order to construct a model, the induction time may be considered as the only detectable macroscopic parameter representative of the nucleation process. Following the general approach reported in the literature for nucleation and crystallization growth [6], the temperature dependence of the induction time (t_i) is given by

$$t_i = K_{t0}\exp[E_{t_2}/R(T - T_g)]\exp[E_{t_1}/R(T_m^{\ominus} - T)] \tag{1}$$

where K_{t0} is a pre-exponential factor. The two exponentials account for the driving forces of nucleation above the glass transition temperature T_g and below the theoretical melting point $T_m^{\ominus}$, E_{t_1} and E_{t_2} being the activation energies of these two contributions. The significance of each term of eqn. (1), with respect to the different driving forces of the nucleation process

TABLE 1

Parameters of the kinetic model (eqns. (1), (9) and (12)); $T_g = 358$ K, $T_m^{\ominus} = 576$ K

	PPS neat resin	PPS matrix composites
n	2.1	1.9
$\ln K_{t0}/(\ln s^{-1})$	−4	−3.2
$E_{t_1}/R/K^{-1}$	460	410
$E_{t_2}/R/K^{-1}$	230	205
$\ln K_0/(\ln s^{-n})$	1.8	4.1
$E_1/R/K^{-1}$	820	900
$E_2/R/K^{-1}$	270	320

which also govern the crystal growth process, will be discussed later. Induction times obtained in isothermal DSC experiments performed at different temperatues have been used to verify the validity of the eqn. (1) model and to compute its parameters. Taking logarithms on both sides of eqn. (1), the representation of $\log t_i$ as a function of $1/(T - T_g)$ and $1/(T - T_m^{\ominus})$ should produce two linear behaviors in the two intervals close to T_g and $T_m^{\ominus}$, respectively. However, as a consequence of the very slow crystallization process in these regions, experimental points were far removed from the T_g and $T_m^{\ominus}$ values expected for linear behavior. A multiple non-linear regression analysis of the experimental data was then performed using a statistical software package (Systat). The parameters of the eqn. (1) model computed with this procedure are reported in Table 1 for both materials studied. Good agreement between the experimental data obtained for the pure PPS polymer and the PPS matrix composite, and the respective model predictions are shown in Figs. 3 and 4. From these results,

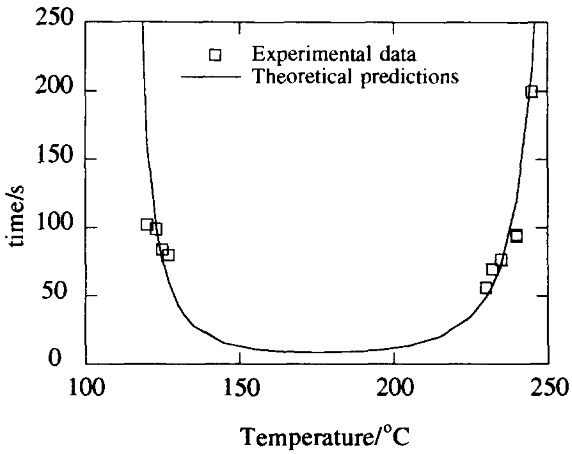

Fig. 3. Temperature dependence of induction times obtained during isothermal crystallization of PPS neat resin.

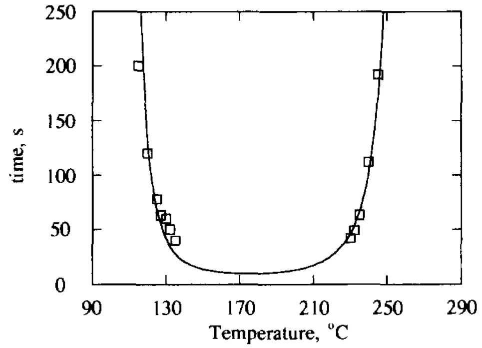

Fig. 4. Temperature dependence of kinetic constants calculated from isothermal and non-isothermal crystallization of PPS neat resin.

it is evident that the temperature range that can be explored is limited by the strong dependence of the induction times on the test temperature and that information provided by non-isothermal experiments should also be considered for full model verification.

In non-isothermal conditions, the induction time is given by the time that verifies the condition

$$\int_0^t \mathrm{d}t/t_i = 1 \tag{2}$$

where t_i is the isothermal induction time given by eqn. (1) and the time $t = 0$ is taken at the melting temperature. Equations (1) and (2) will be combined with the crystal growth model in the following section.

Crystal growth

The development of crystallinity is associated with the exothermic peaks shown in Figs. 1 and 2. These peaks can be integrated to compute the mass fraction of crystallinity X_{mc} assuming a proportionality between the rate of crystallization and the heat flow measured by DSC [8, 13]

$$X_{\mathrm{mc}} = 1/Q_{\mathrm{f}} \int_0^t \mathrm{d}Q/\mathrm{d}t\,\mathrm{d}t \tag{3}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the heat rate developed at a given time during the crystallization process and Q_{f} is the heat of fusion of a perfect crystal, taken as 77.5 J g^{-1} from the X-ray data reported by Brady [15]. In the case of the composite, the value of $\mathrm{d}Q/\mathrm{d}t$ is referred to the actual mass fraction of matrix, reported to be 0.34. The relationship between X_{mc} and the crystallinity volume fraction X_{vc} is

$$X_{vc} = X_{mc}\rho_a/[\rho_c - X_{mc}(\rho_c - \rho_a)] \tag{4}$$

where $\rho_a = 1320\,\mathrm{kg\,m^{-3}}$ is the density of the amorphous phase and $\rho_c = 1430\,\mathrm{kg\,m}^{-}3$ is the density of the crystalline phase, as reported by Dawson and Blundell [16].

As reported extensively in the scientific literature [6], macrokinetic models of the isothermal crystallization of semi-crystalline polymers have generally been obtained from the Avrami equation

$$X_r(t) = X_{vc}/X_\infty = 1 - \exp[-kt^n] \tag{5}$$

where X_r is the relative volume fraction of crystallinity referred to the final amount of crystallinity developed in the same thermal conditions at long times (X_∞), n is the Avrami exponent, k is the kinetic constant, and t the crystallization time. Following the same approach, non-isothermal crystallization processes have been traditionally represented obtaining integral or differential expressions of the classical Avrami model with a temperature-dependent kinetic constant. In particular, Nakamura et al. [17] proposed the integral expression

$$X_r(t) = 1 - \exp\left[-\int_0^t K(T)\,\mathrm{d}t\right]^n \tag{6}$$

$K(T)$ is related to the Avrami constant in eqn. (5) through the relation $K(T) = k(t)^{1/n}$. Equation (6) reduces to the Avrami equation under isothermal conditions. A differential expression of the Nakamura model, more suitable for kinetic studies and for process modelling, was obtained by Patel and Spruiell [14]

$$\mathrm{d}X_r/\mathrm{d}t = nK(T)(1 - X_r)\{\ln[1/(1 - K_r)]\}^{(n-1)/n} \tag{7}$$

Another integral expression developed by Kamal and Chu [18] was later applied to the non-isothermal crystallization of PEEK by Velisaris and Seferis [19]

$$X_r = 1 - \exp\left[-\int_0^t k(T)nt^{n-1}\,\mathrm{d}t\right] \tag{8}$$

Differential expressions for the crystallization rate are more suitable for process modelling purposes and can be more easily related to calorimetric data. Moreover, the use of time as an explicit variable in the differential model allows a better verification of the influence of the induction time model on the overall crystallization process. Therefore, the differential form proposed by Lin [20] will be adopted in this study

$$dX_r/dt = nk(T)(1 - X_r)t^{(n-1)} \tag{9}$$

Patel and Spruiell [14] recently analyzed the available methods describing non-isothermal crystallization in the framework of process modelling. They concluded that an overprediction of non-isothermal data can be attributed to the fact that traditional kinetic models do not account for the induction time due to the nucleation process.

As expressed above, the non-isothermal model of Lin (eqn. (9)) is adopted in this work, combined with the induction time model given by eqn. (1). Therefore, the overall crystallization is modelled considering heterogeneous nucleation and growth of crystals as series processes. In order to complete the model, the temperature dependence of the kinetic constant in eqn. (9) must be provided. Considering that the crystallization kinetic constant is proportional to the crystal linear growth rate G [7], its temperature dependence was recently described [21] on the basis of the theory developed by Hoffman et al. [7]

$$k = k_0 \exp[-E_2/R(T - T_g)] \exp[-E_1/R(T_m^{\ominus} - T]) \tag{10}$$

where k_0 is a pre-exponential factor. The first exponential accounts for the increase in the molecular mobility in the highly viscous region above the glass transition temperature T_g that induces the cold crystallization process, while the second accounts for the driving force of crystallization, given primarily by the degree of undercooling $(T_m^{\ominus} - T)$ with respect to the theoretical melting point $T_m^{\ominus}$.

The exponent n and kinetic constant k in eqn. (9) were calculated using the experimental results obtained in isothermal conditions. Thermogram data were processed in terms of crystallinity volume fraction computed following eqns. (3) and (4) and then applying the classical linearization of the Avrami equation (eqn. (5)) [13]. Data corresponding to several isothermal tests were analyzed using the regression software (10 data sets for the neat resin and 12 data sets for the prepreg were used). The results of the regression analysis were given in terms of the kinetic constant ($k(T)$ in eqn. (9)) and the average value of the crystallization index n (see Table 1) for both materials studied. Then, crystallization rate data measured in non-isothermal experiments were analyzed according to eqn. (9), assuming the value of n calculated previously and obtaining $k(T)$ as a function of temperature (six data sets obtained at different cooling rates were analyzed for each material). Kinetic constants obtained in isothermal conditions and at constant cooling rates were then used to verify the validity of eqn. (10) and to compute its parameters. The procedure described for calculation of the parameters of eqn. (1) was also applied in this case. Moreover, the kinetic constants obtained from isothermal experiments are appropriately weighted in the regression analysis in order to account for the different

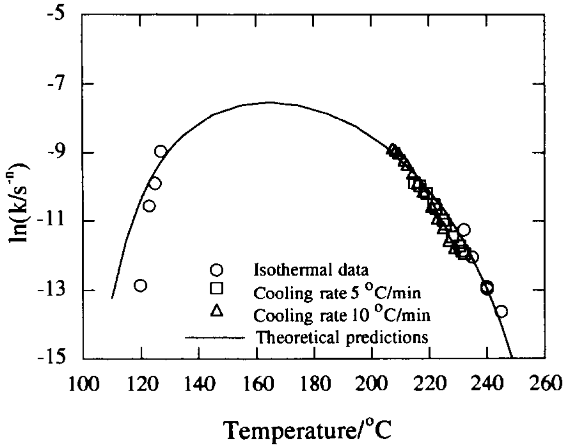

Fig. 5. Comparison between experimental data (points) and model predictions (lines) during isothermal cold crystallization and melt crystallization of PPS neat resin.

number of experimental data sets obtained in isothermal and non-isothermal conditions. Kinetic constants obtained from isothermal and non-isothermal experiments and the results of eqn. (10) compare well in Figs. 5 and 6 for the PPS film and PPS matrix composite respectively. It is also possible to observe that only a limited number of experimental data can be obtained in isothermal experiments over the two narrow temperature ranges (cold crystallization and melt crystallization), while kinetic constant values calculated from non-isothermal DSC experiments cover a wider temperature range. The results of Figs. 5 and 6 confirm the ability of the simplified eqn. (10) model to represent the temperature dependence of the crystallization behavior.

Further verification of the complete kinetic model given by eqns. (1), (2), (9) and (10), using the parameter values computed by linear regression

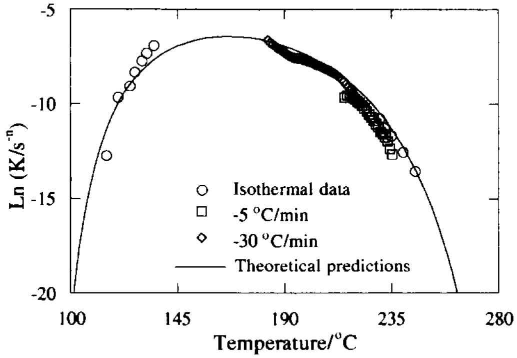

Fig. 6. Comparison between experimental data (points) and model predictions (lines) during crystallization at constant cooling rate of PPS neat resin.

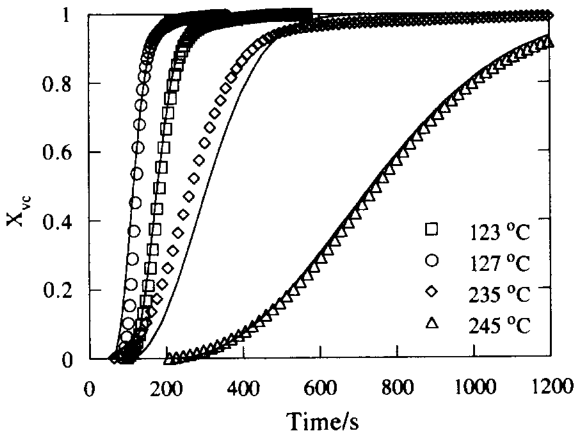

Fig. 7. Temperature dependence of induction times obtained during isothermal crystallization of PPS matrix composite.

reported in Table 1, are presented in Figs. 7–10 where a reasonable agreement between experimental and theoretical curves for the degree of crystallization as a function of time and temperature, is shown for isothermal and non-isothermal processes conducted on both materials studied. It can be seen that the onset of crystallization is well-predicted by the induction time model in both isothermal and non-isothermal experiments, indicating that the nucleation process is correctly represented by this macrokinetic approach. The full model shows a very good agreement with experimental data obtained under very different thermal conditions, providing a fundamental tool for the study of the processing of semi-crystalline thermoplastic matrix composites.

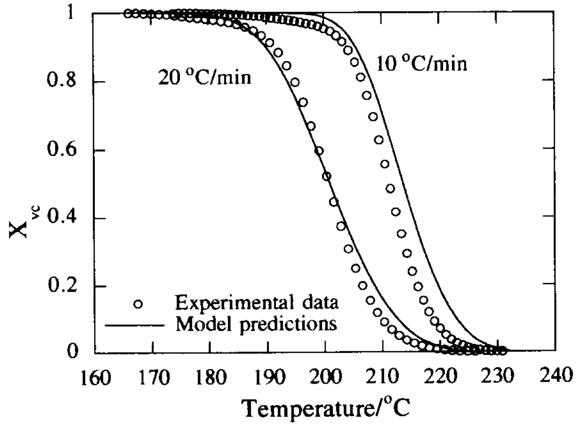

Fig. 8. Temperature dependence of kinetic constants calculated during isothermal and non-isothermal crystallization of PPS matrix composite.

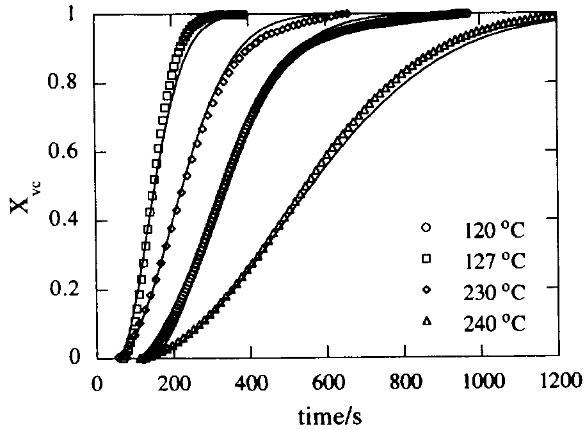

Fig. 9. Comparison between experimental data (points) and model predictions (lines) during isothermal cold crystallization and melt crystallization of PPS matrix composite.

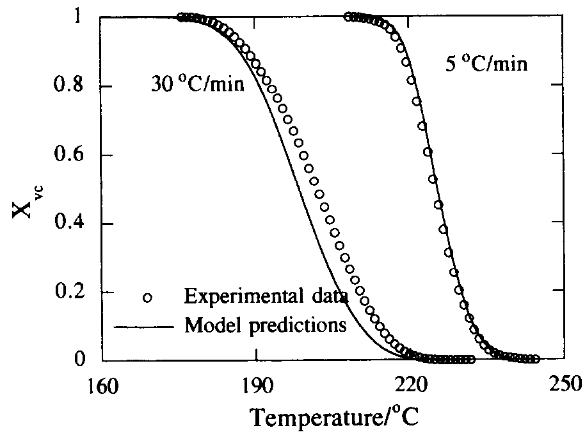

Fig. 10. Comparison between experimental data (points) and model predictions (lines) during crystallization at constant cooling rate of PPS neat resin.

Times-temperature-transformations

Solid-state phase transformations governed by slow kinetic processes are usually studied in metallurgy using plots called TTT (time–temperature–transformations) for isothermal processes or CCT (continuous cooling transformations) when a constant cooling rate is applied [22]. The same kind of approach has been used by Enns and Gillham [23] for the chemorheology of thermosetting matrices in order to predict gelation and vitrification phenomena during cure of composite matrices. Also, the crystallization kinetics of polymers may be better understood using this kind of approach, as reported by Spruiell and White [24]. However, the TTT and CCT diagrams reported in these papers are only a qualitative

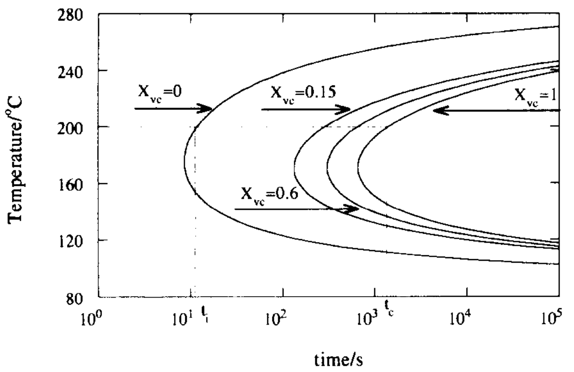

Fig. 11. Time–temperature–transformation (TTT) diagram for the PPS neat resin.

representation of the experimentally observed behavior and only give information on the onset time of crystallization.

The model presented in this paper can be used to build TTT and CCT plots. A TTT diagram for the crystallization of the neat PPS polymer studied is reported in Fig. 11. The first curve from the left represents the beginning of crystallization and it is obtained as the locus of points given by eqn. (1). The curves corresponding to a given degree of crystallization, i.e. $X_r = 0.15$, $X_r = 0.6$ and $X_r = 1$, are computed by application of eqns. (1), (9) and (10). At a fixed temperature, a horizontal line gives, at the first intersection, the time t_0 to each the onset of the crystallization process ($X_r = 0$) according to the induction time model. The kinetic model for crystal growth then provides the time needed to reach different degrees of crystallization and, finally, the time (t_f) for full crystallization ($X_r = 1$). Obviously, the theoretical time required for $X_r = 1$ is infinite; therefore the curve corresponding to full crystallization was calculated for $X_r = 0.99$. Regarding their practical application for polymer processing operations, TTT plots provided by the material suppliers, for each semi-crystalline polymer or composite matrix, could represent a fundamental tool with which to determine the best process conditions. It should be noted that the information given in these TTT plots includes extrapolated data obtained in the region where no experimental data are available.

CONCLUSIONS

A macrokinetic model for the crystallization behavior of polymers and polymeric matrix composites has been presented. The model, accounting for the induction time due to nucleation and adopting a simple expression for the temperature dependence of the kinetic constant, is able to predict the crystallization behavior under isothermal and non-isothermal conditions, including cold crystallization and melt crystallization. The theoretical results are in good agreement with experimental calorimetric data obtained over a wide range of thermal conditions for pure PPS polymer and PPS matrix composite. Finally, the time–temperature–transformation plots constructed from the model developed for isothermal (TTT) conditions, provide a fundamental tool for understanding the crystallization behavior of semi-crystalline matrices and for determining the most suitable processing conditions.

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REFERENCES

1 I.M. Ward, Mechanical Properties of Solid Polymers, Wiley, New York, 1971.
2 J.M. Kenny, A.D'amore, L. Nicolais, M. Iannone and B. Scatteia, SAMPE J., 25 (1989) 27.
3 J.M. Kenny, L. Torre, L. Nicolais, M. Iannone and C. Voto, in J. Brandt, H.L. Hornfield and M. Neitzel (Eds.), Advanced Materials and Structures from Research to Application, Proc. 13th Eur. SAMPE Conf., Basel, Germany, 1992.
4 J.M. Kenny, A Maffezzoli and L. Nicolais, Polym. Compos., 5 (1991) 1.
5 J.M. Kenny and A. Maffezzoli, Compos. Polym., 4 (1991) 12.
6 B. Wunderlich, Macromolecular Physics, Academic Press, New York, 1976.
7 J.D. Hoffman, G.T. Davis and J.I. Lauritzen, The rate of crystallization of linear polymers with chain folding, in N.B. Hannay (Ed.), Treatise on Solid State Chemistry, Vol. 3, Plenum Press, New York, 1976, Chap. 7.
8 A. Maffezzoli, J.M. Kenny and L. Nicolais, Thermochim. Acta, 199 (1992) 133.
9 Y. Lee and R.S. Porter, Polym. Eng. Sci., 26 (1986) 633.
10 G.P. Desio and L. Rebenfeld, J. Appl. Polym. Sci., 44 (1992) 1989.
11 G.P. Desio and L. Rebenfeld, J. Appl. Polym. Sci., 44 (1992) 2005.
12 A.J. Lovinger, D.D. Davis and F.J. Padden, Polymer, 26 (1985) 1595.
13 J.M. Kenny and A. Maffezzoli, Polym. Eng. Sci., 31 (1991) 607.
14 R.M. Patel and J.E. Spruiell, Polym. Eng. Sci., 31 (1991) 730.
15 D.J. Brady, J. Appl. Polym. Sci., 20 (1976) 2541.
16 P.C. Dawson and D.J. Blundell, Polymer, 21 (1980) 577.
17 K. Nakamura, K. Katayama and T. Amano, J. Appl. Polym. Sci., 17 (1973) 1031.
18 M.R. Kamal and E. Chu, Polym. Eng. Sci., 23 (1983) 27.
19 C. Velisaris and J.C. Seferis, Polym. Eng. Sci., 26 (1986) 1574.
20 C.C. Lin, Polym. Eng. Sci., 23 (1983) 113.
21 A. Maffezzoli, J.M. Kenny and L. Nicolais, J. Mater. Sci., in press.
22 L.H. Van Vlack, Elements of Material Science, Addison-Wesley, Reading, MA, 2nd edn., 1964.
23 J.B. Enns and J.K. Gillham, J. Appl. Polym. Sci., 28 (1983) 2567.
24 J.E. Spruiell and J.L. White, Polym. Eng. Sci., 15 (1975) 660.