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A kinetic model that fits nicely isothermal and non-isothermal bulk crystallizations of polymers from the melt

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ABSTRACT

A model describing the low temperature solid state phase transformation kinetics observed in a metal organic framework by differential scanning calorimetry (DSC) at several cooling rates is modified so that the reaction rate is now expressed as a function of time and temperature. Thus, when applied to ramp data, the new model exactly matches the former one but, additionally, it allows to explain isothermal data. The new model is tested for primary crystallizations of two polymers from the molten state, using DSC data, cooling ramp experiments at several cooling rates and isothermal experiments. Good fittings were obtained at all the varied experimental conditions with both polymers. The model makes use of three fitting parameters with physical meaning: an upper critical temperature, T_c, an energy barrier, and a reaction-order, $n + 1$. Additionally, and previously to perform the kinetic fitting, the dependence of the time to the maximum crystallization rate peak on the isothermal temperature was investigated. That dependence was found to follow a simple model which makes use of two parameters related to the limits of the temperature range in which the crystallization may occur. The polymers used in this work were a commercial extruded polyamide and pristine syndiotactic polypropylene.

1. Introduction

Differential scanning calorimetry (DSC) has been largely used for analysis of crystallization, melting and curing processes. Temperature-modulated DSC (TMDSC) has proved to be a very useful technique to understand thermal events where standard DSC fails to separate some overlapping processes [1,2]. In general, when there are not evident overlapping events, standard DSC is used for kinetic study of crystallizations, curing reactions and other transitions. It was applied to identify metal organic framework (MOF) transitions and some trials were done to explain the kinetics of the change of phase [3]. Some of that trials did not result convincing because of lacking of a suitable baseline which lead to a misinterpretation of an apparent overlapping of first and second order transitions [4,5].

In order to determine the kinetic parameters of discrete solid-state reactions, model fitting and model-free procedures are amongst the most used. Other approaches include time–temperature superposition kinetics [6] and master plots [7,8]. The conventional model-fitting approach assumes a fixed mechanism throughout the reaction, involving the fitting of conversion-time data or rate of conversion-time data to some chemically-based models to determine reaction orders, rate constants, and the activation energy from the Arrhenius equation [9]. A way to improve the goodness of fit consists in flexibilizing the model by introducing additional parameters, but it may compromise its physical significance [9]. Crystallization of amorphous materials and other solid state transformations involving nucleation and growth are often described by the Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [10–15]. Model-free kinetics performs an isoconversional

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analysis on data taken at three or more heating rates, where activation energy is allowed to vary with temperature [16]. Thus, model-free methods allow for a change of mechanism during the course of a reaction. Their suitability for obtaining activation energy values without modelistic assumptions is one of the reasons for their extensive use [17–23]. However, model-free methods have some disadvantages, and a reaction model is usually needed for a complete kinetic description of any solid-state reaction [23,24]. It is also important to notice that the model-free kinetic approach is usually applied in the context of the traditional kinetic description based on the kinetic triplet, A, E, and $f(\alpha)$ or $g(\alpha)$ [25]. In that context, the temperature dependence is described by the Arrhenius equation

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E}{R \cdot T}\right) \cdot f(\alpha)$$

where A and E, the pre-exponential factor and the activation energy, respectively, are Arrhenius parameters and R is the gas constant. Thus, in practice, the term free refers only to the conversion dependence, but not to the temperature dependence, which is almost universally assumed to be described by the Arrhenius equation. Nevertheless, it would be very risky to apply that model to cases where there is no evidence that the temperature dependence is accurately described by the Arrhenius equation. In such a situation, the A and E values estimated from the model would make no sense. In the case of non-isothermal crystallization kinetics, the expression for the crystallized fractional volume contains a function of the initial temperature, and modifications on thermoanalytical models have been proposed to include that initial temperature effect [26]. On the other hand, the issues involved in modeling of the solid state transformation kinetics, like heating or cooling rate, can exert a crucial influence on the kinetic outcome and a general methodology for non-isothermal transformations was proposed [27]. On the other hand, the reliability of the signal under analysis is a crucial aspect for any kinetic analysis and obtaining a reliable baseline by means of a careful calibration is of course necessary [28,29].

Fundamentals of crystallization kinetics were conveniently explained by several authors [30–32]. The existing knowledge can be summarized as: (1) The kinetics of crystallization in general and of polymers in particular is known to be non-Arrhenius, it involves two energy barriers, nucleation and diffusion, and depends on supercooling. (2) For crystallization in general a good starting model is that by Fisher and Turnbull, which derived an expression for the absolute rate of nucleation in condensed systems [33]. (3) For flexible polymers, the crystallization kinetics is well described by the Hoffman–Lauritzen theory, which is derived from the Fisher–Turnbull model [34–36]. The Lauritzen–Hoffman theory explains the kinetics of crystallization in molecular terms, for linear flexible macromolecules which are crystallized from the melt into chain folded lamellae. This theory constitutes perhaps the most comprehensive and widely used methodology to interpret and model the crystallization behavior of a large number of polymers. This theory was also considered a good starting point for better explaining the crystallization behavior of rigid chain systems like polyimides [37]. The theory has evolved substantially since it was first proposed and has incorporated several new concepts in order to broaden the scope of its predictions and also to address the objections of other workers in the field [38]. Nevertheless, explanation for primary nucleation and hence bulk crystallization kinetics was still not completely addressed [37]. In spite of Hoffman–Lauritzen theory being well physically grounded, Avrami analysis, which can be easily applied, is the most popular method for obtaining bulk crystallization kinetics information [10,31]. Unfortunately, this method has often been utilized without recognizing the assumptions and limitations of such an analysis, resulting in wrongful interpretations of experimental data [37]. It was reported that isothermal crystallizations of syndiotactic polypropylene and blends of poly(ethylene terephtalate) and poly(methyl methacrylate) are conveniently described by the Urbanovici–Segal and Avrami models [39,40].

It is well accepted in the literature [17,25] that the bulk crystallization rate parameters relate, in one way or another, to the primary nucleation rate I and/or the subsequent crystal growth rate G, the temperature-dependence of the bulk rate parameter can accordingly be quantified and described. Even though the temperature-dependence of the parameters I and G are known to have a different temperature-dependence, the bulk crystallization rate parameters have often been taken to have a similar temperature-dependence to that of the subsequent crystal growth rate G, written in the context of the original Lauritzen and Hoffman secondary nucleation theory (LH theory) [36,38], which can be expressed as

$$\Psi(T) = \Psi_0 \cdot \exp\left(-\frac{A}{R \cdot (T_c - (T_g - C))} - \frac{B}{T_c(\Delta T) \cdot f}\right)$$

where $\Psi(T)$ and Ψ_0 are the respective crystallization rate parameters and the pre-exponential parameter, respectively. A is a parameter related to the activation energy characterizing the molecular diffusion across the melt/crystal interface, while B is a parameter related to the secondary nucleation. T_g is the glass transition temperature, C is the parameter which determines the temperature where the cessation of long-range molecular motion is expected (i.e. $T_g - C$) and is often taken to be either ca. 30 K or ca. 50 K below the glass transition temperature, R is the universal gas constant, delta T is the degree of undercooling, and finally f is a factor used to correct for the temperature-dependence of the heat of fusion. Some of the current developments on polymer crystallization are concerned with which conditions are necessary to nucleate the crystallization process, how experimental conditions affect the reentries of the chains in the lamellae, how the lamellar thickness depends on the number of chains in the crystal [41], and the crystallization of block copolymers with more than one crystallizable block [41–44].

A recent work on the kinetic analysis of complex solid-state reactions by a deconvolution procedure demonstrated that some fitting functions may properly fit the kinetic curves independently of the kinetic model followed