Property modelling

On the Kissinger equation and the estimate of activation energies for non-isothermal cold crystallization of PET

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The activation energy for nonisothermal cold crystallization of polyethylene terephthalate (PET) and its blends with 1% polystyrene (PS) and 1% styrene-acrylonitrile copolymer (SAN) were measured based on differential scanning calorimetry (DSC). The Kissinger method was used to compute the activation energies in all cases, obtaining mean values of 120, 100, and 85 kJ/mole for neat PET, PET/1%PS and PET/1%SAN. A modified Kissinger procedure is proposed to estimate activation energies in polymer systems in which the relative crystallinity - measured at constant heating rates - can be correlated by the Ozawa model with a temperature-independent exponent. Values of the activation energy of 115 and 160 kJ/mole were obtained for cold crystallization of PET in the PET/1%PS and PET/1%SAN blends using the modified Kissinger procedure.

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1. Introduction

The activation energy of a chemical reaction is defined as the minimum amount of energy required to activate the molecules of the reactant to a condition in which they can undergo the chemical transformation. In terms of the transition-state theory, the activation energy is the difference in energy content between the activated or transition-state configuration and the reactant their initial configuration. Activation energy can be thought of as the height of the energy barrier separating two minima of potential energy (of reactants and products of the reaction). For a reaction to advance at a measurable rate, an appreciable number of reactant molecules should have energy equal to or greater than the activation energy in the conditions of the reaction. Under these conditions, the rate constant, that is, the factor of the reaction rate that depends on temperature, and not on the concentration of reactants and products, can be represented by an Arrhenius expression:

\[ k = k_0 \exp\left(-\frac{E_a}{RT}\right) \]  

where \( k_0 \) is a pre-exponential factor, \( E_a \) is the activation energy (energy per mole), \( T \) is the temperature in the absolute scale, and \( R = 8.315 \) J/K mole is the universal gas constant. The parameters \( k_0 \) and \( E_a \) depend on the process in question, but are independent of the temperature. These concepts, while strictly speaking valid only for simple one-step chemical reactions, can be generalized to complex multistep reactions - considering the rate-controlling step - and many physical processes. For polymeric systems, activation energy is a parameter used to investigate many chemical and physical transformations, such as crystallization, reticulation, degradation, decomposition, etc. The effect of additives, pigments, fillers, and other resins may be analyzed in terms of activation energies [1–8].

Thermal analysis techniques, in particular differential scanning calorimetry (DSC), are widely used to acquire data of time, temperature and heat flow absorbed or released during the process under investigation. Several procedures have been developed to calculate activation energies [9–14]. Among them, the Kissinger method has been extensively...
used to study polymer crystallization during the heating of substantially amorphous samples of semicrystalline polymers, a process known as cold crystallization [15,16].

Recently, generalized activation energy, a function of temperature or conversion, has been defined for complex processes [17–19]. However, the classical concept of activation energy as a single number characterizing the process (even if approximately so) irrespective of processing conditions or extent of reaction, has not completely lost its appeal.

In the present work, the Kissinger method is applied to the investigation of the energy barrier for the cold crystallization of the semicrystalline thermoplastic polyethylene terephthalate (PET) and blends of PET with small amounts of the amorphous, immiscible polymers polystyrene (PS) and a copolymer of styrene and acrylonitrile (SAN). PET is widely used in many industrial applications, such as bottles for the packaging industry, fibers for the clothing industry, and devices for the transport industry, in which crystallinity developed during processing plays an important role. PS and the SAN are polymers widely used in the packing, micro-electronics and house devices industries. Experimental evidence shows that the addition of small amounts of PS or SAN has a significant effect in controlling the cold crystallization of mostly amorphous PET samples in a similar way as an anti-nucleating agent does, but with no damage in the mechanical properties, any formulation that difficult the crystallization of PET, increasing the required supercooling and/or decreasing the crystallization rate will have a significant impact on the operating window of process that are affected by the crystallinity of the material. Process such as blow of containers, extrusion film blowing, and fiber forming are examples of these processes [20–26]. Along with the “classic” Kissinger method, a reformulated Kissinger method is suggested to obtain a modified activation energy for the cold crystallization conducted at constant heating rates for systems in which the experimental data can be modeled following Ozawa’s theory [27].

2. Experimental

2.1. Materials

Bottle grade PET, trade name Rhopet S78, was supplied by Rhodia (Brazil) with an intrinsic viscosity $[\eta] = 0.78 \, \text{dL/g}$ and weight-average molar mass $M_w = 48 \, \text{kg/mol}$. Injection grade PS and SAN, trade names Styron 649D and Luran 358N, were purchased from Dow (Brazil) and from BASF, respectively. Preliminary DSC scans of the polymers in Fig. 1 showed glass transitions at 70°C, 95°C and 107°C corresponding to PET, PS and SAN; an exothermic cold crystallization peak at and an endothermic melting peak of PET. Complete absence of crystallinity is observed for PS and SAN.

2.2. Methods

Before mixing, the polymers were oven dried under forced air circulation to remove humidity and prevent PET degradation during processing. PET was dried at 120°C for 6 hours, and PS and SAN at 80°C for 14 hours. The blends were prepared in a Haake Rheomix 600 laboratory internal mixer fitted with high intensity (roller type) rotors for 10 minutes, with the chamber wall kept at 265°C and the nominal speed of the rotors set at 60 rpm. Immediately after mixing, the melt was quenched in iced water to minimize PET crystallization and obtain substantially amorphous samples.

The nonisothermal cold crystallization of PET, PET/PS and PET/SAN blends with 1% of PS or SAN (by weight) was investigated using a differential scanning calorimeter Shimadzu DSC-50. Glassy samples, 5 to 8 mg in weight, were heated from room temperature to 300°C at ten different rates: 1, 2.5, 5, 7.5, 10, 15, 20, 30, 40, and 50°C/min. All test samples were wrapped in aluminum foil to get better heat transfer [28].

3. Theoretical background

Kissinger [15] developed a procedure to estimate the activation energy in physical or chemical processes from data obtained at several nonisothermal tests conducted at constant heating rates (constant during each test, different among tests). The conditions for the validity of Kissinger approach are:

(a) The expression of the rate of reaction $c$ as a function of temperature $T$ and conversion $x$ is separable, that is, may be written as a product of two factors: a kinetic constant $k$, which is a function only of temperature, and a function $f$ of the conversion but not of the temperature:

$$c = \frac{dx}{dt} = k(T)f(x)$$

(b) The kinetic constant is an exponential function of the reciprocal of the temperature, Eq. (1).
(c) Tests are conducted at constant heating rate $\Phi = dT/dt > 0$; the method cannot be applied to processes that occur during cooling [9].

(d) The rate of reaction at constant heating rate $\Phi$ as a function of temperature has a relative maximum in the interval under study; that is, there is a peak temperature $T_p$ for which $dc/dT = 0$ and $d^2c/dT^2 < 0$. It is open to question how to treat systems that for some values of heating rate show multiple peaks and for others single peaks.

(e) The rate or variation of the kinetic function $f(x)$ at the peak is a negative constant $q = (df/dx)_{p} < 0$.

Under these conditions, Kissinger demonstrated that, for a series of isothermal tests:

$$\phi E_a \left(\frac{d}{1/T_p}\right) = -qk_0 \exp\left(-\frac{E_a}{RT_p}\right)$$  \hspace{1cm} (3)

or:

$$\frac{d \ln (\phi/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R}$$  \hspace{1cm} (4)

According to Eq. (4), a plot of $\ln(\phi/T_p^2)$ versus $1/T_p$ (Kissinger plot) leads to a straight line with slope equal to $-E_a/R$. Kissinger method is strictly valid only if all five conditions above, (a) to (e) are met. Frequently, compliance is assumed or proven to be only approximate. In usual applications, peak temperatures $T_p$ are obtained directly from the output of DSC tests conducted at different constant heating rates $\Phi$. The Kissinger method provides a simple and direct (model-free) way to estimate the activation energy $E_a$ for the nonisothermal cold crystallization of polymers.

Ozawa [27] proposed a model to correlate the relative crystallinity $x$ during nonisothermal crystallization of a polymer from a series of tests conducted at different (but constant during each test) heating or cooling rates $\Phi = |dT/dt|$:

$$x = 1 - \exp(-\kappa \phi^{-m})$$  \hspace{1cm} (5)

where the Ozawa parameter $\kappa$ is a function of temperature, $\kappa = \kappa(T)$, and the Ozawa exponent $m$ is a constant, independent of the temperature. In addition to having some theoretical foundation (it can be obtained from Nakamura’s isokinetic assumption [9,28] as the limiting case for constant heating rate), Ozawa’s model has the unique characteristic among other macrokinetic nonisothermal models of having the parameter as a function of temperature.

The differential form of Ozawa’s model, the crystallization rate corresponding to Eq. (4) is:

$$\frac{dx}{dt} = \left. \frac{dx}{d\phi} \right|_{\phi} \phi^{-m}(1-x)$$  \hspace{1cm} (6)

This may further be developed expressing $\Phi$ as a function of $\kappa$ and $x$ according to Eq. (4):

$$\frac{dx}{d\tau} = \kappa^{1/m} \left. \frac{d\ln \kappa}{d\tau} \right|_{\phi} (1-x) \left( \ln \frac{1}{1-x} \right)^{1-1/m}$$  \hspace{1cm} (7)

Eq. (6) correspond to a first-order process for which $q = -1$. Eq. (7) involves the so-called Avrami-Efremov kinetics [10,11] for which $q = -1$; for example, for a symmetric peak ($x_p = 0.5$), $q = -1.13$ for $m = 1$ and $q = -1.03$ for $m = 4$. For constant Ozawa exponent equations (6) and (7) are in accordance with Kissinger conditions (a), (c), (d) and (e); agreement with condition (b) is checked a posteriori: a linear relationship in the plot of Kissinger is taken as proof.

Eq. (6) suggests an alternative way to estimate an activation energy. The equivalent of Kissinger’s Eq. (3) for a process modeled according to Ozawa and conducted at constant heating rate is:

$$\phi E_a \left(\frac{d}{1/T_p}\right) = -k_0 \phi^{-1-m} \exp\left(-\frac{E_a}{RT_p}\right)$$  \hspace{1cm} (8)

where $k_0$ and $E_a$ are defined by the expression:

$$\left. \frac{dx}{d\tau} \right|_{\phi} = k_0 \phi^{-1-m} \exp\left(-\frac{E_a}{RT}\right)$$  \hspace{1cm} (9)

The equivalent of Eq. (4) is now:

$$\frac{d \ln (\phi^{m}/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R}$$  \hspace{1cm} (10)

According to Eq. (10), a plot of $\ln (\phi^{m}/T_p^2)$ versus $1/T_p$ should lead to a straight line with slope equal to $-E_a/R$. The parameter $E_a$ is a modified activation energy, different in general, from activation energy $E_p$.

If Ozawa exponent is a function of temperature, the differential form of Ozawa’s model is not separable; for example, the equivalent of Eq. (6) in this case is:

$$\frac{dx}{dt} = \left. \frac{dx}{d\phi} \right|_{\phi} \kappa^{1/m}(1-x) \left( \ln \frac{1}{1-x} \right)^{1-1/m}$$  \hspace{1cm} (11)

Eq. (11) cannot be separated into the product of two functions, one of temperature alone and the other of conversion (relative crystallinity) alone. The Kissinger method should not be applied in this case.

Finally, while using Kissinger procedure to estimate the activation energy for cold crystallization of polymers, the following considerations must be taken under advice:

- Activation energies may be estimated by other procedures, even if the data fail to meet Kissinger conditions. The Kissinger method is a very convenient way to estimate it, but the concept of activation energy is far more general than the limited assumptions of this particular method.
- Complex processes such as polymer crystallization may not be well represented by a single activation energy, which assumes that the same mechanism prevails from the onset ($x = 0$) to the end of the process ($x = 1$).

4. Results and discussion

DSC raw data in the form of heat flow ($J$) versus time ($t$) or temperature ($T$) were integrated in the time interval
corresponding to the cold crystallization event, from a start point \( t_1 \) to end point \( t_2 \) (visually determined and using a straight virtual baseline \( J_0 \) between them) to obtain the relative crystallinity \( x \) (fraction crystallized) and the crystallization rate \( c \) computed as:

\[
c = \frac{dx}{dt} = \frac{|J - J_0|}{E_0}
\]

where \( E_0 \) is the gross latent heat of crystallization:

\[
E_0 = \int_{t_1}^{t_2} [J(t') - J_0(t')] \, dt'
\]

Relative crystallinities and crystallization rates may be expressed as functions of time or temperature, taking into consideration that, at constant heating rate \( \Phi = \frac{dT}{dt} \), temperature is a linear function of time.

Fig. 2 shows the normalized nonisothermal cold crystallization peaks of PET, PET/1%PS and PET/1%SAN determined at different heating rates [30–36]. Addition of a small amount of amorphous immiscible polymer results in a delay of cold crystallization of the matrix. Thus, PS and SAN behave as anti-nucleant or retardant agents as far as the cold crystallization of PET is concerned. While the degree of crystallinity is not significantly affected by the addition of PS or SAN, the rate of crystallization diminishes, resulting in broader and shorter cold crystallization peaks when compared with the neat PET crystallization peaks [20–22,25]. Even although PS is an apolar and SAN a polar polymer, both have the same effect on the cold crystallization of PET, at least at the low level, 1%, tested in this work. Table 1 lists the peak crystallization temperature for all heating rates tested.

Fig. 3 presents the Kissinger plots based on the data of Table 1. From the slope of the straight lines in the plots, the following values of the activation energy were obtained: \( E_a = 120 \pm 12 \, \text{kJ/mole} \) for neat PET, \( E_a = 100 \pm 14 \, \text{kJ/mole} \) for PET/1%PS, and \( E_a = 85 \pm 8 \, \text{kJ/mole} \) for PET/1%SAN. The expected uncertainty of the activation energy is in the range of 9.5–13%, an acceptable level, as the repeatability and reproducibility of DSC measurements is not better than 6 and 8%, respectively [1,2].

However, the data in Fig. 3 are not well represented by straight lines and the linear Kissinger relationship was forced upon them. The slopes in Fig. 3 increase as the temperature decreases (or \( T_p^{-1} \) increases), suggesting a variable, temperature dependent activation energy. For example, for neat PET crystallization at 110–120°C an activation energy of 165 kJ/mole may be more appropriate than the average value of 120 kJ/mole estimated over the temperature interval 110–140°C, while at 130–140°C a value of 85 kJ/mole may be better, supported by the experimental data (broken lines in Fig. 3). Since the relative crystallinity increases with the temperature during the cold crystallization process, the effective activation energy may be considered as a function of the conversion, as suggested in the literature [37–46].

The DSC data for the cold crystallization of PET and the two blends at different heating rates were correlated according to the Ozawa model, Eq. (5), to obtain the corresponding

<table>
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<th>Table 1</th>
<th>Peak temperature for non isothermal cold crystallization of PET.</th>
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<tr>
<td>PET</td>
<td>( \Phi ) (C/min)</td>
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<tr>
<td>PET/1%PS</td>
<td>( \Phi ) (C/min)</td>
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<tr>
<td>PET/1%SAN</td>
<td>( \Phi ) (C/min)</td>
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<td>148.6</td>
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parameters as functions of temperature in the intervals of 120–135 °C for neat PET, 120–145 °C for the blends. The results may be found elsewhere [20–22,25]. Fig. 4 shows Ozawa’s exponent m as a function of temperature.

Fig. 4 shows neat PET Ozawa’s exponent is strongly dependent on temperature for the whole interval tested, being four times higher at 120 °C (m ~ 1) than at 135 °C. On the other hand, Ozawa’s exponent for the cold crystallization of PET in the blends, while showing a drop at on the lower temperatures tested, display an (approximately) constant exponent for T > 130 °C: m = 1.53 for PET/1% PS and m = 2.27 for PET/1% SAN.

According to the equivalence between isothermal Avrami and nonisothermal Ozawa models [29,30], the Ozawa exponent m describes some characteristics of crystalline entities during the crystallization. If homogeneous nucleation and diffusion controlled crystal growth are assumed the value of m = 1.53 for PET/PS blends suggests one-dimensional crystal growth geometry and the value of m = 2.27 suggests two or tri-dimensional crystal geometry.

Fig. 5 presents plots of ln $\phi^n / T^2_p$ versus 1 / $T_p$ for the two blends using only tests in which $T_p > 130°$ (heating rates greater than 5 °C/min), a condition in which the Ozawa’s exponent may be assumed approximately constant, independent of temperature. From the slope of the straight lines in the plots, the following values of the modified activation energy were obtained: $E'_a = 115 ± 20$ kJ/mole for PET/1%PS and $E'_a = 160 ± 28$ kJ/mole for PET/1%SAN.

5. Final considerations

The Kissinger method has been applied to obtain the activation energy for the cold crystallization of PET in neat resin, and in blends with small amounts of PS and SAN. A modification of the classic procedure was presented, applicable to processes conducted at constant heating rates that can be modeled according to Ozawa procedure, in systems with little secondary crystallization and narrow variation of the morphological structure of the crystallites, leading to almost constant values of the m exponent. The Kissinger is a very simple and fast method to obtain mean activation energies, useful in comparative studies, specifically those taking place during constant heating rates with a defined peak temperature. An analysis of Kissinger plots may also show the activation energy dependence on temperature, and allows computing local values of the activation energy for different stages of the process. In this way, it may be a simpler alternative to complex isoconversional kinetic analysis, which is related to the extent of phase transformation, valid at least for a preliminary screening. Isoconversional methods lead to temperature dependent
activation energy. Some researchers believe that the activation energy should be a constant, independent of temperature, in order to be a meaningful kinetic parameter [6,7].

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