

NON-ISOTHERMAL CRYSTALLIZATION OF POLYVINYLALCOHOL-CO-ETHYLENE

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Non-isothermal crystallization of polyvinylalcohol-co-ethylene with different ethylene contents was studied. Several models were used to predict the crystallization behavior of these materials under non-isothermal conditions at a constant cooling rate. Kinetic parameters determined from isothermal data were employed. Experimental data were in accordance with model prediction at low cooling rate and relative degree of crystallization lower than 0.8, but it did not fit at high cooling rate.

Kinetic parameters obtained by using a non-linear regression method, i.e. Kamal's model and Dietz's modification, were able to describe better the non-isothermal crystallization behavior of the studied materials. The full model, that takes into account the induction and growth of the crystal during cooling under non-isothermal conditions was used to obtain a continuous cooling transformation diagrams for polyvinylalcohol-co-ethylene.

Finally, non-isothermal models, coupled with the proposed expressions for induction time and kinetic constant, were used to represent the development of crystallinity during the processing of the polymer.

Keywords: crystallization, modellization, polyvinylalcohol-co-ethylene

Introduction

The study of the crystallization kinetics of polymers under different thermal conditions is very important for the analysis and design of processing operations. In fact, during fabrication, the polymeric material suffers one or more cycles of heating, melting, cooling, and crystallization that determine the development of the polymer structure and the physical properties of the final product [1].

The control of the temperature profile during cooling in the final stage of a process determines the development of a specific morphology, which influences the final properties of the material. Cooling rate is therefore important and it can be adjusted to modulate the level of crystallinity of a polymer. However, the modeling of non-isothermal crystallization implies the knowledge of isothermal phenomena which gives information on the kinetics and morphology developed at each crystallization temperature [2–4].

The behavior of semicrystalline polymers during non-isothermal crystallization from the molten state is of increasing technological importance because real industrial processes such extrusion and film forming usually proceed under dynamic, non-isothermal conditions. The aim of the paper was to study the influ-

ence of the ethylene content on the non-isothermal crystallization behavior of polyvinylalcohol-co-ethylene and to obtain a global macrokinetic model for analysis and design of processing operations. The theoretical models allowed the description of the crystallization behavior of these materials during processing under non-isothermal conditions.

Crystallization models

The relative degree of crystallinity; X_r , is defined as the area under the crystallization peak at a given temperature divided by the total area under the peak and it is related to the quantity of the transformation from the amorphous polymer to crystalline polymer at a given time. The macrokinetic of the isothermal crystallization of semicrystalline polymers has traditionally been approached using the classical Avrami equation [5–8]:

$$X_r = 1 - \exp(-kt^n) \quad (1)$$

where X_r is the relative degree of crystallinity, n is the Avrami exponent, k is the overall kinetic constant and t is the time of crystallization. The parameters n and k can be used to explain qualitatively the nucleation mechanism, morphology and overall crystallization rate on polymers.

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In the last year, many expressions obtained from general Avrami theory have been utilized to model the crystallization kinetics under non-isothermal conditions. One of first attempts to obtain an expression to study the crystallization process under non-isothermal conditions has been proposed by Ozawa [9]. This expression allows the determination of the Avrami exponent which is related to the crystalline morphology of polymer. In the literature there are many examples of application of this model [6], and it is mainly used to analyze the effect of different fillers during the crystallization process of polymers [10–11]. However, the Ozawa analysis requires values of relative degree of crystallinity at a given temperature for different constant cooling rates. Hence, it is not possible to include a wide range of cooling rates and the temperature range over which the analysis can be applied is very narrow. On the other hand, this model cannot be applied to predict the development of crystallinity under real processing conditions because it assumes constant cooling rate.

Kamal and Chu proposed that non-isothermal crystallization can be approached using an empirical expression derived from Avrami model and obtaining integral expression with a temperature dependent kinetic constant [12–14].

$$X_r = 1 - \exp\left[-\int_0^t k(T) n t^{n-1} dt\right] \quad (2)$$

or using temperature as independent variable, for each constant cooling rate, the Eq. (2) can be rewritten as:

$$X_r = 1 - \exp\left[-\int_{T_0}^T k(T) n \left(\frac{T_0 - T}{\beta}\right)^{n-1} \frac{dT}{\beta}\right] \quad (3)$$

where the time variable was substituted by $(T_0 - T)/\beta$, being β the cooling rate.

As it was reported in the literature for process modeling, a differential form of Kamal and Chu model (refer to Eq. (2)) is more useful than its integral form.

$$\frac{dX_r}{dt} = nk(T)(1 - X_r)t^{n-1} \quad (4)$$

In all the cases the models can be reduced to the Avrami equation in isothermal conditions. For different materials k had been written following the Arrhenius relationship with temperature [6, 7, 15–17]:

$$k = k_0 \exp\left(-\frac{E_a}{R(T_m^0 - T)}\right) \quad (5)$$

where E_a is the activation energy for crystallization process, k_0 is the pre-exponential constant, T_m^0 is the theoretical melting temperature, and R is the gas constant, $(T_m^0 - T)$ is the thermodynamic driving force for

crystallization because the crystallization rate is zero at the theoretical melting point.

Dietz proposed a modification of Kamal differential equation that considers the effects of secondary crystallization or diffusional effect that occurs at high degree of crystallinity [18]. Taking into account these effects, Eq. (4) can be written as:

$$\frac{dX_r}{dt} = nk(T)(1 - X_r)t^{n-1} \exp\left[-\frac{aX_r}{1 - X_r}\right] \quad (6)$$

where the empiric parameter a lies between zero and one. When $a=0$ the Dietz's equation is reduced to the Kamal and Chu model. The Kamal and Chu equation and the Dietz's modification can be easily used to predict the crystallization process under non-isothermal condition.

These models can be applied only to crystal growth after nucleation. The nucleation is a thermally activated phenomena and their effect can be detected by isothermal DSC experiment where a signal can be observed only after a delay (induction time) attributed to the formation of nuclei of critical size [1]. However, the effect of the induction time is more complex in non-isothermal crystallization experiments where a time – temperature superposition is verified. So, the induction time cannot be determined directly from non-isothermal experiments. On the other hand it is fundamental to know the induction time in order to determine the onset time for the crystal growth. The initial condition in a non-isothermal simulation is given by the induction time calculated as the sum of the contributions of several isothermal temperature steps evaluated from the isothermal crystallization experiments. The dependency of the isothermal induction time with temperature can be expressed as:

$$t_i = K_i \exp\left(\frac{E_i}{R(T_m^0 - T)}\right) \quad (7)$$

where K_i is the pre-exponential factor and E_i is the activation energy for the nucleation process.

The non-isothermal induction time (t_{ni}), can be calculated in terms of a dimensionless parameter Q , ranging from 0 to 1, defined as:

$$Q = \int_0^{t_{ni}^*} \frac{dt^*}{t_i} \quad (8)$$

where t_i is the isothermal induction time given by Eq. (7). Numerical integration of Eq. (8) is performed by taking $t^*=0$ at the theoretical melting temperature (T_m^0). The value $t^*=t_{ni}^*$ at which $Q=1$ represents the non-isothermal induction time. The Eqs (6) and (7) can be combined with the crystal growth model to obtain a global macrokinetic model that allows to pre-

dict the development of crystallinity during the processing of the polymer.

Experimental procedure

PVOH-co-ethylene with three different ethylene molar content: 32, 38 and 44% supplied by Sigma-Aldrich S.A., were used to study the non-isothermal crystallization and the effect of ethylene on PVOH crystallization.

The non-isothermal crystallization kinetics was measured by calorimetric analysis using a differential scanning calorimeter (DSC) PerkinElmer Pyris 1, operating from 30 to 450°C under nitrogen atmosphere. The samples were first heated from room temperature to 250°C, at a heating rate of 10°C min⁻¹. Then, the samples were maintained at 250°C for at least 10 min in order to allow the complete melting of these materials, and finally, they were cooled at different cooling rates (5, 10 and 20°C min⁻¹). During cooling, samples crystallized. The relative degree of crystallinity X_r which developed on cooling to temperature T was obtained as:

$$X_r = \frac{\int_{T_0}^T \left(\frac{dH_c}{dT} \right) dT}{\int_{T_0}^{T_\infty} \left(\frac{dH_c}{dT} \right) dT} \quad (9)$$

where T_0 and T_∞ represent the initial and final crystallization temperatures, respectively, and H_c is the crystallization enthalpy.

The theoretical melting temperature (T_m^0), the induction time parameters: activation energy (E_i) and pre-exponential constant (K_i), and kinetic parameter obtained from isothermal tests: activation energy (E_a), pre-exponential factor (k_0) and Avrami index (n) were taken from the literature and listed in the Table 1 [19].

Results and discussion

Figures 1 show the crystallization curves obtained during cooling stage after melting of PVOH-co-ethylene used at different cooling rates. It is possible to observe the exothermic peak temperature (T_p) and the initial crystallization temperature (T_0) shifts to lower

temperatures as the cooling rate increases irrespectively of the ethylene content. This behavior is a consequence of cooling rate affects on the nucleation process. As the cooling rate increases the motion of polymer chain cannot follow the cooling temperature and thus polymer crystallization begins at lower temperatures. The values of T_p and T_0 , at different cooling rate and ethylene content are shown in Table 2. For a given cooling rate, it is possible to see that when the ethylene content increases T_p and T_0 decrease. This is a consequence of the decrease on the theoretical melting temperature (T_m^0) with the increase of ethylene molar contents in the copolymer [19].

By numerical integration presented on Eqs (8) and (9) and using the induction parameter obtained from isothermal analysis it is possible to predict the onset crystallization temperature (T_0) for the different constant cooling rates and ethylene contents used in this study. The predicted values of T_0 are also shown in the Table 2. The predicted values are very close to experimental ones, indicating the effectiveness of the selected approach.

In the literature it has been reported that kinetic parameters of crystallization process obtained from isothermal data can be used to predict the non-isothermal crystallization phenomena. For the beginning of non-isothermal crystallization process, the onset temperature, T_0 , determined from induction parameters was considered as initial condition (refer to Eqs 7 and 8) [1]. The prediction of non-isothermal crystallization from isothermal data using the Kamal model (refer to Eq. (3)) are compared with the non-isothermal experimental data obtained from Eq. (9) in the Fig. 2 for the copolymers with ethylene molar contents of 32, 38 and 44, respectively. Experimental data and model predictions have an acceptable agreement at low cooling rates, but at the highest cooling rates, these models are not able to predict experimental data. The Kamal model using the isothermal kinetic parameters over predicts the non-isothermal data, especially at high cooling rate. It was also found that the model does not fit the experimental results at high cooling rates due to heat transfer from the calorimeter oven to the specimen, or due to diffusion problem or secondary crystallization.

As an alternative method we proposed to fit non-isothermal data using directly differential Kamal model (Eq. (4)). A non-linear regression analysis

Table 1 Parameters obtained from isothermal tests from [19]

Ethylene/%	K_i/s	$E_i/kJ mol^{-1}$	k_0/s^{-n}	$E_a/kJ mol^{-1}$	$T_m^0/^\circ C$	n
32	$2.96 \cdot 10^{-4}$	2.75	687.1	3.03	187.0	2.2
38	$7.40 \cdot 10^{-5}$	3.00	364.2	2.72	182.6	2.1
44	$4.12 \cdot 10^{-5}$	3.30	200.7	2.85	176.3	2.2

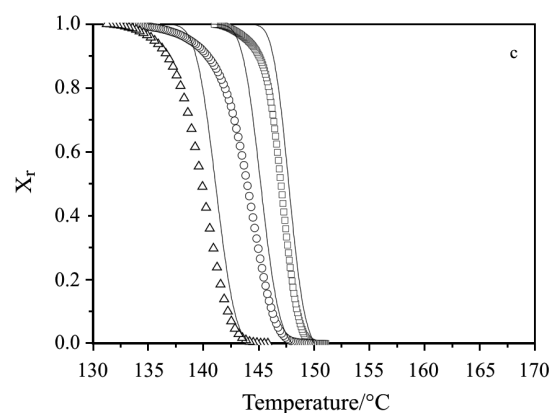
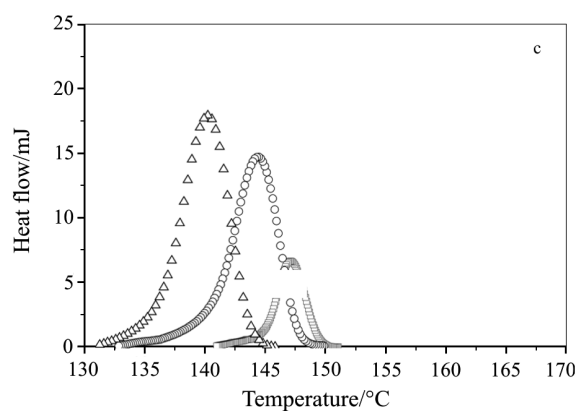
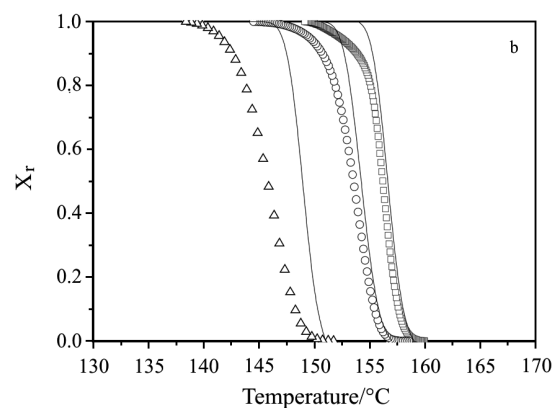
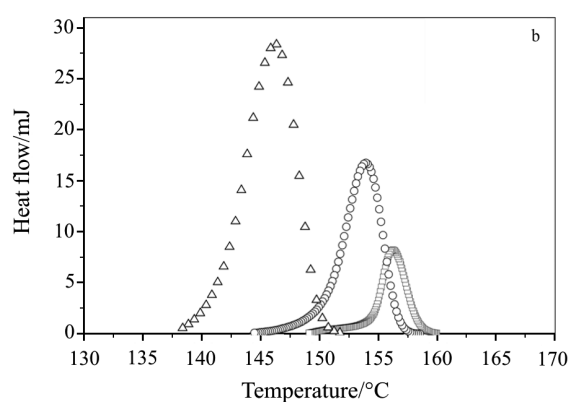
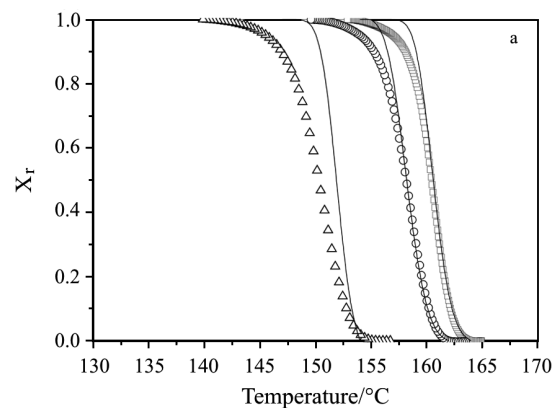
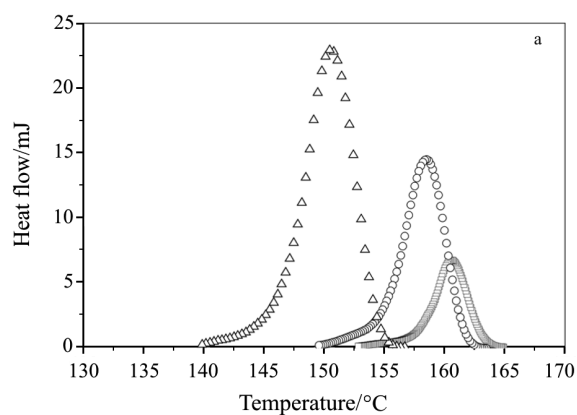


Fig. 1 Non-isothermal crystallization of different PVOH-co-ethylene used at different cooling rates: a – PVOH- 32% ethylene; b – PVOH- 38% ethylene and c – PVOH- 44% ethylene. \square – $5^{\circ}\text{C min}^{-1}$, \circ – $10^{\circ}\text{C min}^{-1}$ and \triangle – $20^{\circ}\text{C min}^{-1}$

Fig. 2 Relative degree of crystallinity as a function of temperature. Experimental data and curves predicted from isothermal data. a – PVOH- 32% ethylene; b – PVOH- 38% ethylene and c– PVOH- 44% ethylene. \square – $5^{\circ}\text{C min}^{-1}$, \circ – $10^{\circ}\text{C min}^{-1}$ \triangle – $20^{\circ}\text{C min}^{-1}$ and — — model

Table 2 Parameters of non-isothermal crystallization of PVOH-co-ethylene

$\beta/^{\circ}\text{C min}^{-1}$	32% ethylene			38% ethylene			44% ethylene		
	$T_p/^{\circ}\text{C}$	$T_{0\text{ exp}}/^{\circ}\text{C}$	$T_{0\text{ pred}}^*/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{0\text{ exp}}/^{\circ}\text{C}$	$T_{0\text{ pred}}^*/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_{0\text{ exp}}/^{\circ}\text{C}$	$T_{0\text{ pred}}^*/^{\circ}\text{C}$
5	160.8	164.0	162.7	156.4	159.0	158.2	147.2	150.0	149.0
10	158.4	162.5	160.4	154.1	157.2	156.2	144.4	149.2	148.3
20	150.5	156.0	154.5	146.3	151.5	151.0	140.3	145.0	144.4

* T_0 determined from induction model (Eqs (6) and (7))

based on the Marquardt method [20] was used to find the best fitting parameters of Eqs (3) and (4). The procedure used in this work provides a single set of kinetic parameters valid for different cooling rates; thus, these parameters can be easily used to model different processing condition.

Figure 3 shows the comparison between experimental data and model prediction using the non-linear regression method. The Kamal model fits experimental data for crystallization degree between 0 and 0.8 and studied cooling rates for all ethylene contents. Better agreement was found with this semi-empirical model, using E_a , k_0 and n as fitting parameters. The kinetic parameters obtained with the best fit are shown on Table 3. There, exists a relationship between the kinetic constant values and the ethylene content: both, the activation energy and the pre-exponential factor increase with ethylene content. However, the obtained results show a decrease in the kinetic constant, $k(T)$, with the increase of the ethylene content. This behavior was also found in isothermal crystallization [19].

As it was explained before the Kamal model fits the non-isothermal data until relative degree of crystallinity of around 0.8. The deviation of the model prediction, from experimental data for crystallization degree is higher than 0.8; this is a consequence of secondary crystallization process or diffusion effects. In order to obtain a good agreement between experimental data and model prediction throughout the complete range of X_r , the Dietz model (Eq. (6)) was used. A single empirical parameter, a , valid for all cooling rates was obtained from samples with different ethylene contents using the same kinetic parameter (E_a , k_0 , and n) obtained previously with Kamal model.

Figures 4 show the comparison between non-isothermal experimental data and predicted curves using the Dietz's model. In this case a good agreement was obtained in all relative degree of crystallinity range. The values of a parameter are also shown in the Table 3.

Coupling the induction time model Eqs (7) and (8) and Dietz's model Eq. (6) it was possible to obtain a full model that represents the experimental data under any cooling conditions. This full model is a very important tool for the study of the processing of semicrystalline polymer.

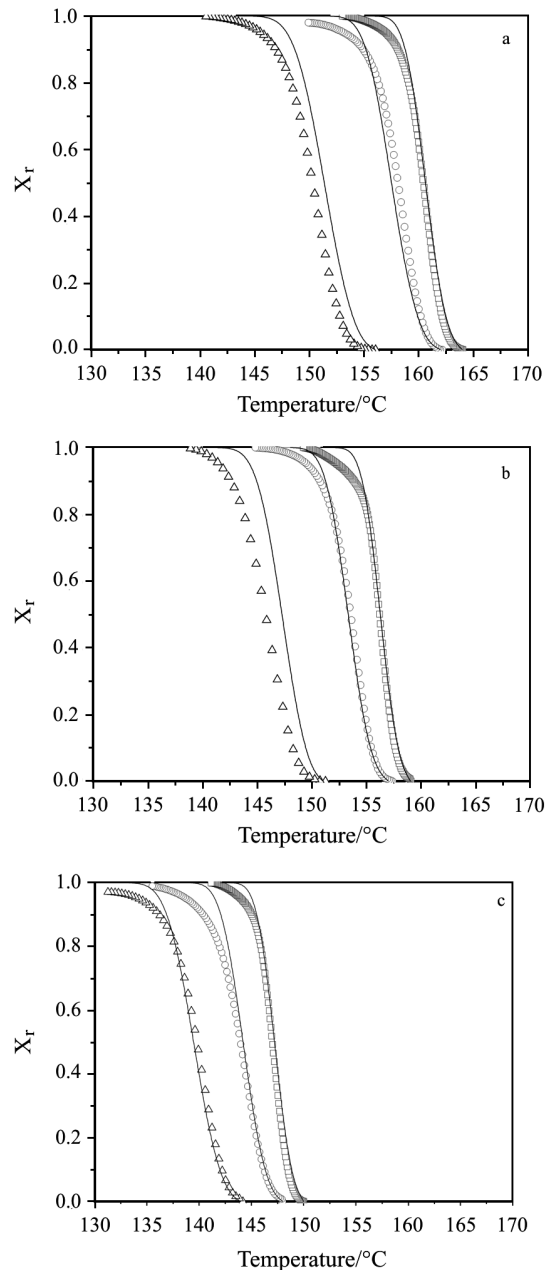


Fig. 3 Relative degree of crystallinity as a function of temperature. Experimental data and curves and values predicted from the Kamal-Chu differential model, using a non-linear multivariable regression method. a – PVOH- 32% ethylene; b – PVOH- 38% ethylene and c – PVOH- 44% ethylene. \square – $5^{\circ}\text{C min}^{-1}$, \circ – $10^{\circ}\text{C min}^{-1}$ \triangle – $20^{\circ}\text{C min}^{-1}$ and — — model

Table 3 Best kinetic parameters obtained with Kamal-Chu and Dietz models using a non-linear regression method

Ethylene/%	k_0/s^{-n}	$E_a/\text{kJ mol}^{-1}$	n	a	$k_{145^{\circ}\text{C}}/\text{s}^{-n}$
32	1.68	1.75	2.05	0.085	$1.12 \cdot 10^{-2}$
38	3.21	1.81	2.01	0.105	$9.82 \cdot 10^{-3}$
44	4.40	2.08	2.03	0.083	$1.49 \cdot 10^{-3}$

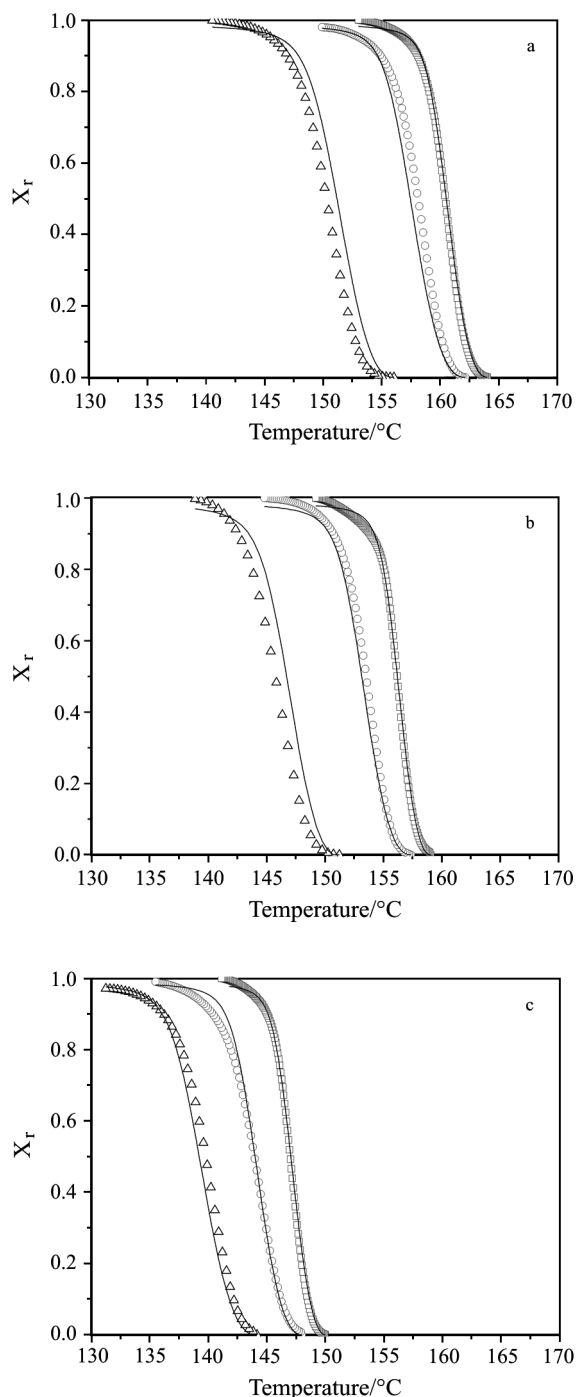


Fig. 4 Relative degree of crystallinity as a function of temperature. Experimental data and curves and values predicted from the Dietz differential model. a – PVOH-32% ethylene; b – PVOH- 38% ethylene and c – PVOH- 44% ethylene. \square – $5^{\circ}\text{C min}^{-1}$, \circ – $10^{\circ}\text{C min}^{-1}$ \triangle – $20^{\circ}\text{C min}^{-1}$ and — — model

The full model can also be applied to obtain phase diagrams that are useful to predict the nucleation and growth of the crystal under a wide range of cooling conditions. Solid-state phase transformations governed by slow kinetic processes are usually stud-

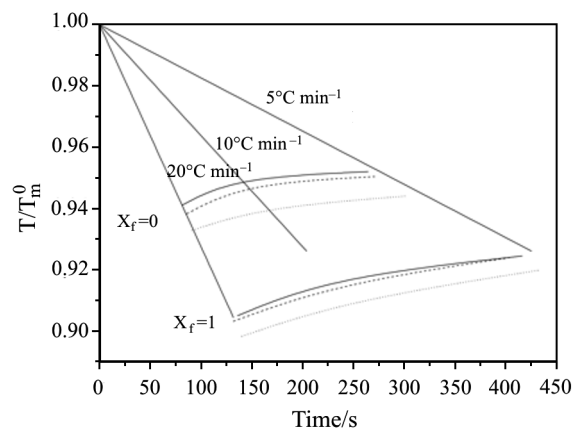


Fig. 5 CCT plots for EVOH: (solid line) 32% ethylene; (dash line) 38 % ethylene and (dot line) 44% ethylene

ied in metallurgy using TTT (time – temperature transformations) plots for isothermal processes [17] or CCT (continuous – cooling transformations) plots when a constant cooling rate is applied [21]. On CCT plots the development of crystallinity as a function of time and temperature is obtained by following a constant cooling rate curve. The complete knowledge of crystallization rate process can be obtained from this kind of approach [22–23]. The crystallinity content as a function of cooling rate can be reported as a fundamental tool for process design and optimization.

The crystallization behavior during constant cooling rate processes (CCT plots) is described on Fig. 5, where curves representing different degrees of crystallization are plotted as a function of time. Each point on these curves has been obtained by integration of the full model at a given cooling rate. Then, the interception of a constant degree of crystallization curve with a constant cooling rate curve represents the time needed for the material to reach the given degree of crystallization under the specific thermal conditions.

Conclusions

Non-isothermal crystallization of polyvinylalcohol-co-ethylene with different ethylene contents was studied.

It was found that the exothermic peak temperature (T_p) shifted to lower temperatures when the cooling rates and ethylene content increased.

By using kinetic parameters obtained from isothermal crystallization process of the same materials, a good agreement between experimental data and model predictions was found at low cooling rate and degree of crystallinity lower than 0.8, but for higher cooling rates and higher degree of crystallinity this model was not able to predict experimental behavior.

The Kamal–Chu differential model, with the Dietz's modification using a non-linear multivariable regression method was used to obtain a better prediction of experimental data. It was found that the kinetic constant $k(T)$ as a combination of parameters depends on the ethylene content. The kinetic constant increases at a given temperature when the ethylene content increases.

The CCT diagram of crystallization provides information about the semicrystalline matrices behavior under different cooling rates, especially on the determination of the crystallinity degree for different processing conditions which is an important tool for process design and optimization.

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List of symbols

t	time of crystallization
k	kinetic constant
X_r	relative degree of crystallinity
T	temperature of crystallization
T_0	onset temperature of crystallization
n	Avrami exponent
k_0	preexponential factor of Avrami constant
R	universal gas constant
E_a	apparent activation energy
T_m^0	infinite-crystal melting point
β	cooling rate
Q	dimensionless parameter ranging from 0 to 1
t_i	isothermal induction time
K_i	preexponential factor for the nucleation process
E_i	activation energy for the nucleation process
t^*	parameter; $t^* = 0$ at the melting temperature (T_m^0). $t^* = t_{ni}$ at, which Q reaches the unity represents the nonisothermal induction time
T_p	The exothermic peak temperature

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