

EVALUATION OF THE MASTER CURVE APPROACH FOR THE NON-ISOTHERMAL CRYSTALLIZATION OF PP/EPR

AVALIAÇÃO DO MÉTODO DA CURVA MESTRE PARA CRISTALIZAÇÃO NÃO-ISOTÉRMICA DE PP/EPR

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ABSTRACT

The purpose of the present work was to test the validity of the Master Curve Approach in order to determine the nonisothermal crystallization constant for a heterophasic polypropylene (PP/EPR). Nonisothermal crystallization experiments were carried out in a DSC at several cooling rates, and the original curves were corrected because of the temperature lag between the samples and the furnace. Through the use of the nonisothermal kinetic crystallization constant, determined by the Master Curve Approach, and the use of the Nakamura equation, the curves of relative crystallinity in relation to temperature were simulated and compared with the corresponding curves obtained from experimental data. A relatively good agreement with the experimental curves was obtained.

Key words: ethylene-propylene rubber, crystallization, master curve approach, heterophasic polypropylene

RESUMO

O objetivo do presente trabalho foi testar a validade do Método da Curva Mestre para a determinação da constante de cristalização não isotérmica para um polipropileno heterofásico (PP/EPR). Experimentos de cristalização não isotérmica foram realizados em um Calorímetro Diferencial de Varredura em várias taxas de resfriamento, sendo as curvas originais corrigidas em relação à defasagem de temperatura entre a amostra e o forno do DSC. Utilizando-se a constante cinética de cristalização não isotérmica determinada pelo Método da Curva Mestre e empregando-se a equação de Nakamura, as curvas de cristalinidade relativa em

função da temperatura foram simuladas e comparadas com as correspondentes curvas obtidas a partir dos dados experimentais, tendo sido obtida uma concordância relativamente boa.

Palavras-chave: elastômero de etileno-propileno, cristalização, método da curva mestre, polipropileno heterofásico

Introduction

Some of the most important industrial polymers are semi-crystalline. So, it is important to incorporate the crystallization phenomenon in simulation programs of polymer processing. In this case, it is necessary to determine the parameters of the kinetic model chosen for describing crystallization process. Recently, Isayev and co-workers (Chan *et al.*, 1995) have proposed the Master Curve Approach, where nonisothermal data of crystallization kinetics at cooling rates between 2 and 40 °C/min obtained from DSC measurements are shifted to obtain a Master Curve of crystallization. From these curves the nonisothermal crystallization rate constant, K , can be determined. This method is similar to the well known time-temperature superposition method (Ferry, 1980), being important that the crystallization process does not present any significant change in the range of temperature where the method will be applied. Therefore, it is necessary to test this method for polymers that could present problems with the several heating and cooling runs in DSC using the same sample, as required by this method. This is the case of the heterophasic polypropylene, as will be discussed later.

Background

The Master Curve Approach is based only on crystallization kinetics experimental data and on the validity of the following expression to express the kinetics:

$$\frac{d\theta}{dt} = K(T)f(\theta) \quad (1)$$

with θ being the degree of crystallinity, T the temperature and t the time. If the general equation (1)

is valid, for a constant degree of crystallinity we have:

$$\frac{\left(\frac{d\theta}{dt}\right)_{ij}}{\left(\frac{d\theta}{dt}\right)_{rj}} = \frac{K(T_{ij})f(\theta_j)}{K(T_{rj})f(\theta_j)} = \frac{K(T_{ij})}{K(T_{rj})} = a_T(T_{ij}) \quad (2)$$

where $a_T(T_{ij})$ is the shift factor at temperature T_{ij} with reference to the temperature T_{rj} , $i: 1,2,3\dots r\dots$ stands for the i -th cooling rate, $j=1,2,3$, denotes the j -th degree of crystallinity. From the equation (2) one can obtain plots of $a_T(T_{ij})$ vs T_{ij} at constant j . If one further picks a temperature T_r among the temperatures T_{rj} as the overall reference temperature, one can shift the plots $a_T(T_{ij})$ vs T_{ij} at constant degree of crystallinity, j , to obtain a single plot of the shift factor as a function of temperature.

From this last curve, $a_T(T_{ij})$ vs T_{ij} , Isayev and co-workers (Chan *et al.*, 1995) have defined the reduced time for nonisothermal crystallization, ξ , with respect to the reference temperature, T_r , as follow:

$$\xi = \int_0^t a_T(T(t')) dt \quad (3)$$

where:

$$a_T(T) = \frac{K(T)}{K(T_R)} \quad (4)$$

The data of θ vs. ξ for different cooling rates should fall on a master curve. The half time of crystallization at the reference temperature, $(t_{1/2})_r$, can be evaluated from the master curve.

Thus, the nonisothermal crystallization rate constant is obtained from the following equation:

$$K(T_R) = \frac{(\ln 2)^{1/n}}{(t_{1/2})_R} \quad (5)$$

where n is the Avrami index, 3 for this case. From $K(T_r)$, $K(T)$ can be determined for the whole temperature range where the shift factor a_T vs. T was taken, by the use of the equation (4). The curve $K(T)$ vs T can then be fitted by the Hoffman e Lauritzen (1976) equation:

$$K(T) = (\ln 2)^{1/n} \left(\frac{1}{t_{1/2}_o} \right) \exp \left(\frac{-U/R}{T - T_\infty} \right) \exp \left(\frac{-K_g}{T\Delta Tf} \right) \quad (6)$$

where $(1/t_{1/2}_o)$ is a pre-exponential factor that includes all terms independent of temperature; U is the activation energy for the transport of crystallizing units across the phase boundary; K_g is the nucleation exponent; $T_\infty = T_g - 30$ K is the temperature below which transport ceases, R is the universal gas constant, $\Delta T = T_m^0 - T$ is the supercooling; $f = 2T / (T_m^0 + T)$ is a correction factor accounting for the reduction in the latent heat of fusion as the temperature is decreased, T_m^0 being the equilibrium melting point.

The differential form of the Nakamura equation (Nakamura, 1973) can be used to simulate the θ vs. T curves, expressed as follows:

$$\frac{d\theta}{dt} = nK(T)(1-\theta)[- \ln(1-\theta)]^{n-1/n} \quad (7)$$

Experimental

The material studied here was a heterophasic polypropylene-ethylene propylene rubber (PP/EPR), with 6.8 % in mol of ethene in the synthesis and MFI = 5.7 g/10min, kindly supplied by BRASKEM S.A.

A Perkin Elmer Calorimeter DSC-7 was used to study the crystallization kinetics. An indium sample was used for calibrating the DSC and the method proposed by Janeschitz-Krieger (Janeschitz-Krieger et al., 1993; Eder and Janeschitz-Krieger, 1993) was used to correct the temperature lag between the DSC sample and the furnace during the cooling runs. It is important to point out that the Master Curve Approach must be used only after this correction procedure. About 5 mg of the material was sealed in an aluminum pan. The sample was heated from the ambient temperature to 200°C and annealed in the molten state for 5 minutes in

nitrogen atmosphere. Then, the sample was cooled at a constant rate (40, 30, 20, 10, 5 e 2.5 °C/min) to 50°C. Following the procedure recommended by Isayev and co-workers (Chan et al. 1995) to get good repeatability for the heat transfer conditions between the furnace and the aluminum pan, the six cooling rates were run in series and the same sample was used for all the six cooling rates without moving the sample.

Results and Discussion

Figure 1 shows the plots of the crystallization rate as a function of the sample temperature. As expected, higher cooling rates lead to larger and wider peaks and lower onset and peak temperatures, as well as higher crystallization rates.

The corrected experimental curves of the figures 1 and 4 and the equation (2) were used to obtain the data of $a_T(T_{ij})$ vs. T_{ij} for various constant degrees of crystallinity, j , resulting on the curves showed in the figure 2. Thus, the reference temperature, T_r , was chosen, and the curves were shifted to obtain the master curve for the shift factor. As can be seen in the figure 3, a relatively good superposition of the kinetic data was obtained. From these data, the reduced time was evaluated by using the equation (3). From the curve of θ vs. ξ , $(t_{1/2})_R$ was obtained and so $K(T_R)$ by the use of the equation (5). $K(T)$ as a function of the temperature was evaluated by the equation (4).

The nonisothermal crystallization rate constant so evaluated could be used, in association with the Nakamura equation (equation (7)), to obtain the plots of the relative crystallinity, θ , as a function of the temperature for the different cooling rates. Figure 4 shows that a relatively good agreement between the experimental and the simulated curves was obtained. It shows that the procedure recommended by Isayev and co-workers (Chan *et al.*, 1995) to get good repeatability for the heat transfer conditions between the furnace and the aluminum pan did not bring problems for this sample. Due to the long annealing times at high temperatures associated to the use of the same sample in all DSC runs, coalescence phenomenon of the EPR rubber phase could occur in this kind of polymer

(Mirabella, 1993; Mirabella, 1994). It could modify the crystallization kinetic (Martuscelli, 1984) from one run to the next and the different non isothermal runs could not fall on the same master curve. Although it was obtained a reasonable fitting between the simulated and the experimental data, the effect on the crystallization kinetics of the possible coalescence of EPR and the possible degradation of the sample due to the repeated annealing at high temperatures should be studied in future works of this polymer.

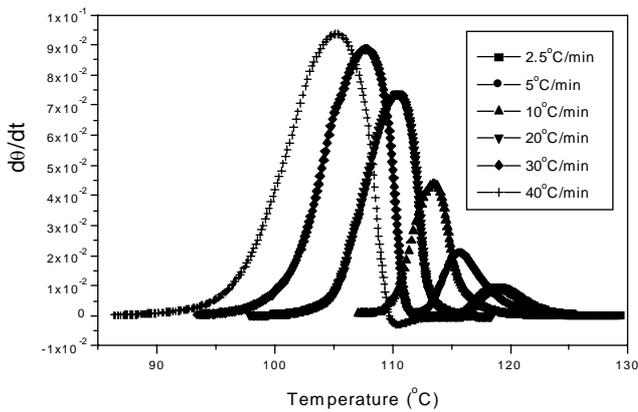


Figure 1- $d\theta / dt$ as a function of the sample temperature at various cooling rates.

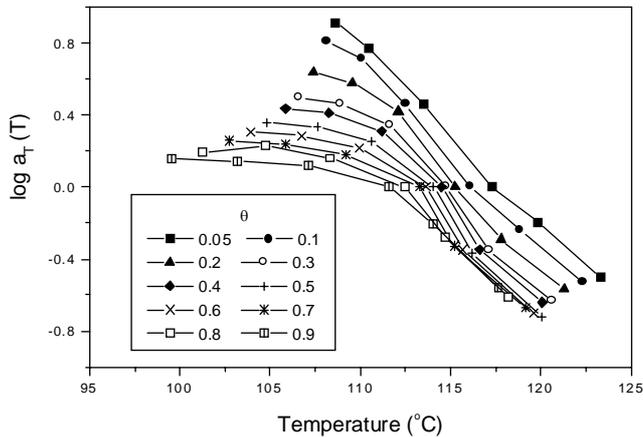


Figure 2- Shift factors as a function of temperature at various degrees of crystallinity.

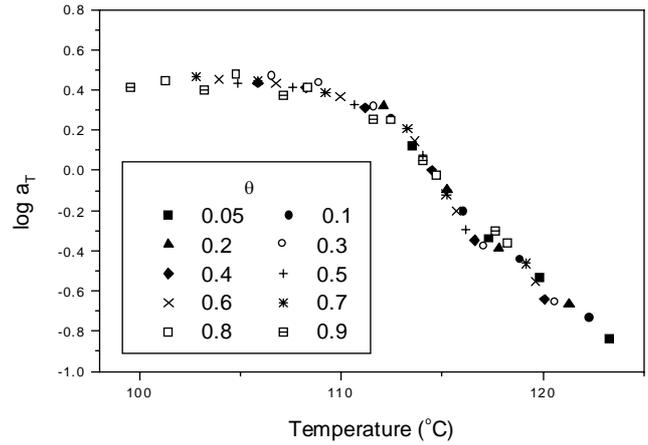


Figure 3- Master curve for the shift factor vs. Temperature for different cooling rates. $T_r = 114.49\text{ }^\circ\text{C}$.

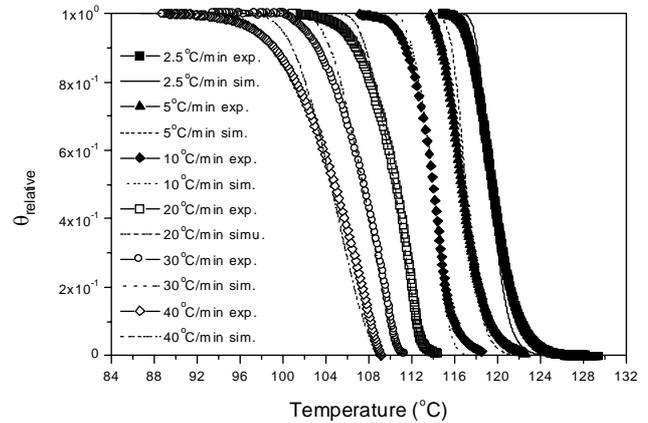


Figure 4- Experimental and simulated plots of relative crystallinity (θ_{relative}) as a function of the temperature. The simulated curves were obtained from the nonisothermal crystallization rate constant ($K(T)$) and the Nakamura equation.

Conclusions

The Master Curve Approach was applied to determine the nonisothermal crystallization rate constant, $K(T)$, as a function of temperature for a heterophasic

polypropylene (PP/EPR). The agreement between the simulated and the experimental curves of q vs. T was relatively good, indicating that the method of the Master Curve Approach was valid for this material.

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