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A new method to determine the Avrami exponent by d.s.c. studies of non-isothermal crystallization from the molten state

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The method reported in this paper is a simple means by which to determine the Avrami exponent, n, after cooling from the molten state of semi-crystalline polymers. This determination, often drudgery, has been significantly simplified, yet remains satisfactorily reliable. It is based on the measurement, from an experimental crystallization exotherm, of the peak maximum and its inflexion points for different cooling rates. Results were tested against the Ozawa theory, and it was found that our method was suitable for a slightly filled or unfilled thermoplastic polymer. However, neither our method nor the Ozawa theory apply when the matrix is reinforced with an efficient nucleating agent. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The behaviour of thermoplastic semi-crystalline polymers during non-isothermal crystallizations from the molten state, is of increasing technological importance, because these conditions are the closest to real industrial processing conditions. The study of non-isothermal crystallization kinetics, from differential scanning calorimetry (d.s.c.) measurements, has been approached in a theoretical way by Ozawa[1]. It allows the kind of nucleation (homogeneous or heterogeneous), and the growth geometry (one-, two-, or three-dimensional growth) to be predicted and quantified by means of a factor, n, called the Avrami exponent. The Ozawa theory is an extension of that of Avrami[2], which considers the case of isothermal crystallizations, basing its mathematical reasoning on an analogy with the propagation of circular waves produced when rain drops fall on a water surface. The shock wave resulting from a drop fall, and the drop itself, are respectively compared to the growth front of the crystalline entity, and to the nucleation germ. Ozawa used this theory, supposing a constant cooling rate, and extended the mathematical derivation proposed by Evans[3] to the case of non-isothermal crystallizations. However, the theory has a certain number of limits. For instance, secondary crystallization of the products is not taken into account, and the exponent n is considered to be constant whatever the temperature. Moreover, effects such as transcrystallization are not considered in the Ozawa theory. It so happens that this particular phenomenon accelerates the average kinetics of transformation, and tends to make up for the volume restriction effects which, on the contrary, slow down crystallization kinetics[4]. As a result, the Avrami exponent, n, has no physical significance any more when strong surface nucleation occurs, because its evolution involves factors with contradictory effects. Therefore, the way it varies when fibres or nucleating agents are added to the bulk polymer become problematic and not easily interpretable.

The determination of n during cooling from the molten state at a constant rate, uses the following equation proposed by Ozawa:

$$[X_V(T)]_U = 1 - \exp\left(-\frac{K(T)}{U^n}\right) \qquad (1)$$

where $X_V(T)$ is the volume fraction of the transformed polymer at a temperature T, U is the cooling rate, and $K(T)$ is the so-called cooling function. The latter only

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varies as a function of temperature. For a given temperature, it depends on the growth geometry of the crystalline entities (one-, two-, or three-dimensional growth), and on the nucleation process (homogeneous or heterogeneous). Ln $K(T)$ is supposed to be a linear function of the temperature.

It appears that in a non-isothermal process, the Avrami exponent may change with the crystallization temperature, the cooling rate and the transformed volume fraction. In the literature, the treatment of experimental results by the Ozawa method uses a linear relation such as

$$\mathrm{Ln}[-\ln(1 - X_{\mathrm{V}}(T))] = \ln K(T) - n \ln U \qquad (2)$$

Equation (2) involves determining transformed volume fractions for different cooling rates at a given temperature. It appears difficult in practice to find more than two or three points at a particular temperature, because of the considerable change in the degree of supercooling with variations in the cooling rate. On the other hand, taking into account the entire crystallization exotherm leads to errors which are in particular due to the superposition of different crystallization regimes (primary and secondary). Indeed, at a given temperature, if we have a primary crystallization regime for any cooling rate, we will always have a secondary crystallization regime for a lower rate. As few authors consider only the beginning of the crystallization in order to obtain consistent results. So, Lopez and Wilkes[5] in the case of polyphenylene sulfide, use crystalline volume fractions lower than 0.5 in order to reduce the effect of spherulite impingement which decreases the crystallization rate, and therefore the value of n by changing the crystallization mechanism. In the same way, Chabert *et al.*[6] limit their investigation of polyamide 66 in the presence of glass fibres, to an exploitation of the beginning of the crystallization peaks (about 30%) in order to improve their results. Monasse and coworkers[7,8] use the average value of n as observed throughout the crystallization temperature range. Moreover, Privalko and coworkers[9,10] showed that incorrect measurement of the temperature T_0 at the beginning of crystallization has a considerable effect on the calculation of $X_{\mathrm{V}}(T)$. Under these conditions, n is particularly affected at the beginning of the phenomenon.

All these remarks support the idea that the Ozawa theory can only be used for temperature domains corresponding to the central parts of the crystallization thermograms.

The method shown in the present paper allows this ambiguity to be excluded, and simplifies appreciably the determination of n. It is based on the experimental observation that the crystallization exotherms essentially have a Gaussian shape. For this reason, only the maximum and inflexion points of the curve need to be considered. This allows us to work with transformation rates where the impingement of the crystalline entities stays low.

In general, the crystallization thermograms obtained in d.s.c. give the transformed mass fraction $X_{\mathrm{W}}(T)$, by partial integration of the exothermal peak at a temperature T. Therefore, such an experimental crystallization curve can be expressed as

$$A_0 \frac{\partial}{\partial T}(X_{\mathrm{W}})_{\mathrm{U}} \qquad (3)$$

where A_0 is the total area of the exothermal peak. The Ozawa relation (equation (2)) using a transformed volume fraction, it is necessary to convert, in a first step, $X_{\mathrm{W}}(T)$ into $X_{\mathrm{V}}(T)$. Knowing ρ_{a}, the density of the amorphous phase, and ρ_{c}, the density of the crystallized phase, $X_{\mathrm{V(T)}}$ is obtained by the following relation:

$$X_{\mathrm{V}}(T) = \frac{X_{\mathrm{W}}(T)\frac{\rho_{\mathrm{a}}}{\rho_{\mathrm{c}}}}{1 - \left[1 - \frac{\rho_{\mathrm{a}}}{\rho_{\mathrm{c}}}\right] X_{\mathrm{W}}(T)} \qquad (4)$$

By this operation, the original d.s.c. curve may be redrawn as a curve which depends on the transformed volume fraction. Assuming a linear dependence between $\ln K(T)$ *versus* temperature as suggested by the theory.

$$\mathrm{Ln} K(T) = aT + b \qquad (5)$$

$$\Rightarrow K(T) = \exp(aT) \times \exp(b) \qquad (6)$$

It is possible to express the value of the extremum of the exothermal curve T_{m} for a given cooling rate U, by finding the zero of the primary derivative of the peak equation, that is to say by resolving the following equation:

$$\frac{\partial}{\partial T}\left(\frac{\partial}{\partial T} X_{\mathrm{V}}\right)_{\mathrm{U}} = 0 \qquad (7)$$

Using equation (1), the resolution of the latter equation leads to equation (8)

$$\frac{\partial}{\partial T}\left[\frac{1}{U^n}\frac{\partial K}{\partial Y}\exp\left(-\frac{K(T)}{U^n}\right)\right] = 0 \qquad (8)$$

$$\Rightarrow \left[\frac{\partial^2 K}{\partial T^2} - \frac{1}{U^n}\left(\frac{\partial K}{\partial T}\right)^2\right] = 0 \qquad (9)$$

From equation (6), we obtain

$$\frac{\partial K}{\partial T} = a \exp(aT + b) \qquad (10)$$

and

$$\partial^2 \frac{K}{\partial T^2} = a^2 \exp(aT + b) \qquad (11)$$

Combining equations (9), (10) and (11) involves a linear relation between T_{m} and $\ln U$

$$T_{\mathrm{m}} = \frac{n}{a}\ln U - \frac{b}{a} \qquad (12)$$

The values of the two inflexion points are obtained from the solution of the secondary derivative of equation (7):

$$\frac{\partial^2}{\partial T^2}\left[\frac{\partial}{\partial T}(X_{\mathrm{V}})_{\mathrm{U}}\right] = 0 \qquad (13)$$

$$\Rightarrow \frac{\partial^3 K}{\partial T^3} - \frac{3}{U^n}\frac{\partial K}{\partial T}\frac{\partial^2 K}{\partial T^2} + \left(\frac{1}{U^n}\right)^2\left(\frac{\partial K}{\partial T}\right)^3 = 0 \qquad (14)$$

Knowing that

$$\frac{\partial^3 K}{\partial T^3} = a^3 \exp(aT + b) \qquad (15)$$

and replacing $\frac{\partial K}{\partial T}$ and $\frac{\partial^2 K}{\partial T^2}$ by their values with equations (10) and (11), it follows that

$$\left(\frac{1}{U^n}\right)^2 \exp[2(aT + b)] - \frac{3}{U^n}\exp(aT + b) + 1 = 0 \qquad (16)$$

The two solutions may be expressed as

$$T_1 = \frac{n}{a}\ln U + \frac{\ln\left(\frac{3-\sqrt{5}}{2}\right)}{a} - \frac{b}{a} \qquad (17)$$

$$T_2 = \frac{n}{a}\ln U + \frac{\ln\left(\frac{3+\sqrt{5}}{2}\right)}{a} - \frac{b}{a} \qquad (18)$$

Theoretically, T_m, T_1, and T_2 as a function of $\ln U$ are linear relations with the same slope $\frac{n}{a}$.

RESULTS

The exploitation of this simple calculus method of the Avrami exponent in non-isothermal conditions was carried out for an isotactic polypropylene filled or unfilled by glass beads or carbon black. All these fillers were uncoated. For such a polymer, the density of the amorphous phase is $\rho_a = 0.852$, and that of the crystallized phase is $\rho_c = 0.935$. The experimental curves were obtained with a DSC-7 Perkin-Elmer, by cooling the samples from the molten state, at varied cooling rates. Prior to this operation, the polymer was maintained for 4 min at above its melting temperature (200°C)[11], in order to destroy the crystallization germs initially present in the bulk. The cooling rates chosen for the investigations were intentionally low. The aim of this choice was to limit the problems due to changes in the crystallization regimes. In such conditions, the crystallization takes place at a relatively high temperature range. Moreover, only the three values T_m, T_1, and T_2, representing the maximum value of the peak and the two inflexion points were considered on the experimental thermogram. Thus optimal conditions were achieved for the thermograms to be used according to the Ozawa theory.

Unfilled isotactic polypropylene

A computer program developed in the laboratory allows us to convert the transformed mass fraction $X_W(T)$ into a transformed volume fraction $X_V(T)$ by applying equation (4) to all the points of the experimental curve. By this operation, a non-isothermal crystallization exotherm may be represented, as in *Figure 1*. The integration of the treated peaks for the different cooling rates used leads to the curves giving the evolution of the transformation ratio as a function of the temperature (*Figure 2*).

From the different crystallization peaks for a cooling rate scale between 2 and 40°C min^{-1}, the values of the temperatures T_1 (first inflexion point), T_m (maximum of the peak), and T_2 (second inflexion point) were determined. According to the theory, these temperatures vary linearly with the cooling rate logarithm (*Figure 3*) when the latter stays low (<10°C min^{-1}). Above this cooling rate, the values of T_1, T_m, and T_2 considerably decrease when $\ln U$ increases, because of the superposition of several crystallization regimes. It was established that under these conditions, the slopes of the three straight lines are identical for the low cooling rates. Moreover, the symmetry of the crystallization exotherms involves the equidistance of the straight lines. Therefore, in a general manner, T_1, T_m, and T_2 (noticed T_i) may be expressed as $T_i = A\ln U + B_i$.

Considering only, for instance, T_1 and T_2, and combining the previous equation with equations (17) and (18), we have to resolve the following simple system:

$$\begin{cases} \dfrac{n}{a} = A \\ \dfrac{\ln\frac{3-\sqrt{5}}{2}}{a} - \dfrac{b}{a} = B_1 \Rightarrow n = A\dfrac{\ln\left(\frac{3-\sqrt{5}}{3+\sqrt{5}}\right)}{B_1 - B_2} \\ \dfrac{\ln\frac{3+\sqrt{5}}{2}}{a} - \dfrac{b}{a} = B_2 \end{cases}$$

From the experimental results presented in *Figure 3*, obtained for unfilled polypropylene, the coefficients A, B_1, and B_2 are respectively calculated as:

$$A = -5.06;\ B_1 = 122.7;\ B_2 = 119.8$$

In these conditions, n is 3.3. This is close to the theoretical value. Indeed, a value of about 3 is characteristic of a heterogeneous nucleation followed by three-dimensional spherulitic growth.

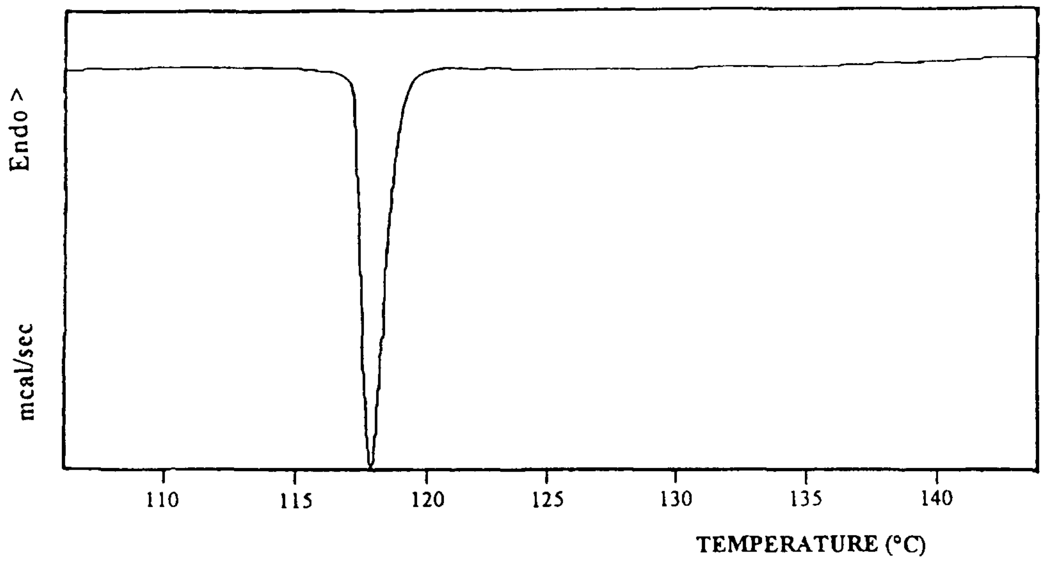

Figure 1 Non-isothermal crystallization exotherm of the unfilled polypropylene for a cooling rate of 2°C min^{-1}

Reinforced polypropylene

It has been demonstrated[11] that, at low concentration, glass fillers in polypropylene are a weak nucleating agent. The polymer therefore behaves as if it were unfilled, and at least at low cooling rates ($<10°C\,min^{-1}$), no preferential nucleation occurs at the filler surface. This fact is widely confirmed by observations in polarized light optical microscopy. However, at greater concentrations, the presence of glass fillers influences the crystallization behaviour of the matrix. Under these conditions, the crystallization exotherms obtained during cooling from the molten state are shifted towards higher temperatures, and this expresses the influence of the reinforcing materials on the heterogeneous nucleation of the polymer. This general behaviour is verified in the case of the materials used for our investigations. *Figures 4* and *5* represent the variations of T_1, T_m, and T_2 as a function of $\ln U$ for the same polypropylene, filled with 5 and 40% of uncoated glass beads respectively. The exploitation of the experimental data for 5% glass filled polypropylene by the Ozawa theory according to our calculus method, is satisfactory for cooling rates lower than $10°C\,min^{-1}$. Within this range of cooling rates, the variation of T_1, T_m, and T_2 as a function of $\ln U$ is always linear, and the straight lines obtained are parallel and equidistant (*Figure 4*). Applying our calculus

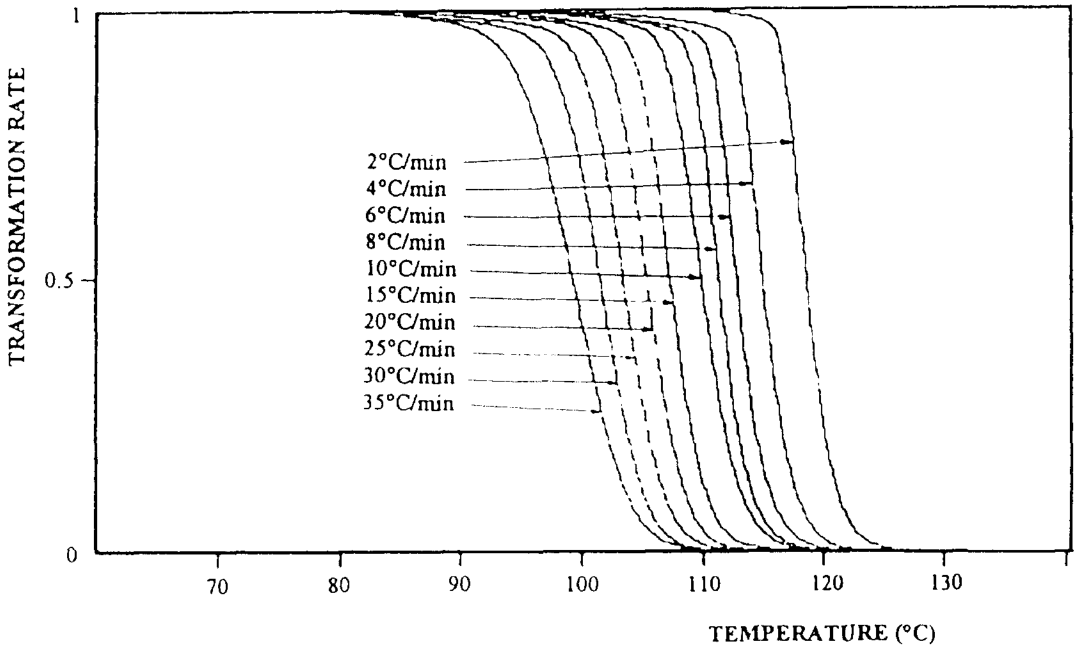

Figure 2 Evolution of the transformed ratio of the unfilled polypropylene as a function of temperature, for different cooling rates

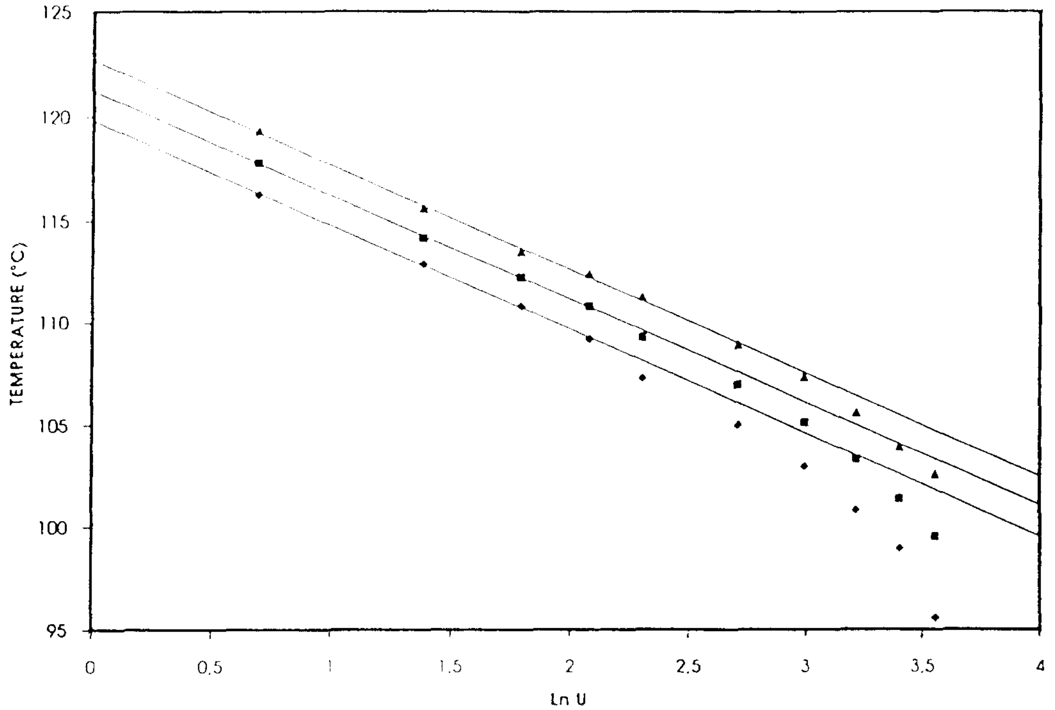

Figure 3 Evolution of T_1 (▲), T_m (■), and T_2 (◆) of the unfilled polypropylene as a function of $\ln U$

method, the Avrami exponent, n, is 2. According to Ozawa, the considerable decrease in n is due to a more heterogeneous nucleation than in the case of the unfilled polypropylene, and to a two-dimensional growth of the crystalline entities. These observations tend to assign an important role to the glass beads in the crystallization behaviour of the polymer, even if this role is not clearly observable in optical microscopy. However, this conclusion is confirmed by the fact that the characteristic crystallization temperatures are consistently higher for a given cooling rate in the case of the reinforced polypropylene.

For a sample containing a greater proportion of filler (40% by mass of glass beads), *Figure 5* shows that the curves T vs $\ln U$ are no longer linear, even for the low cooling rates. This implies that the influence of the glass beads has become predominant, and is therefore difficult to interpret by the Ozawa theory. The conclusions are the same if the polypropylene is reinforced by carbon black. It is clear that such fillers play a major nucleating role for this polymer, even at low concentrations. This is confirmed in *Figure 6* where straight lines characteristic of the variation of T_1, T_m, and T_2 diverge considerably.

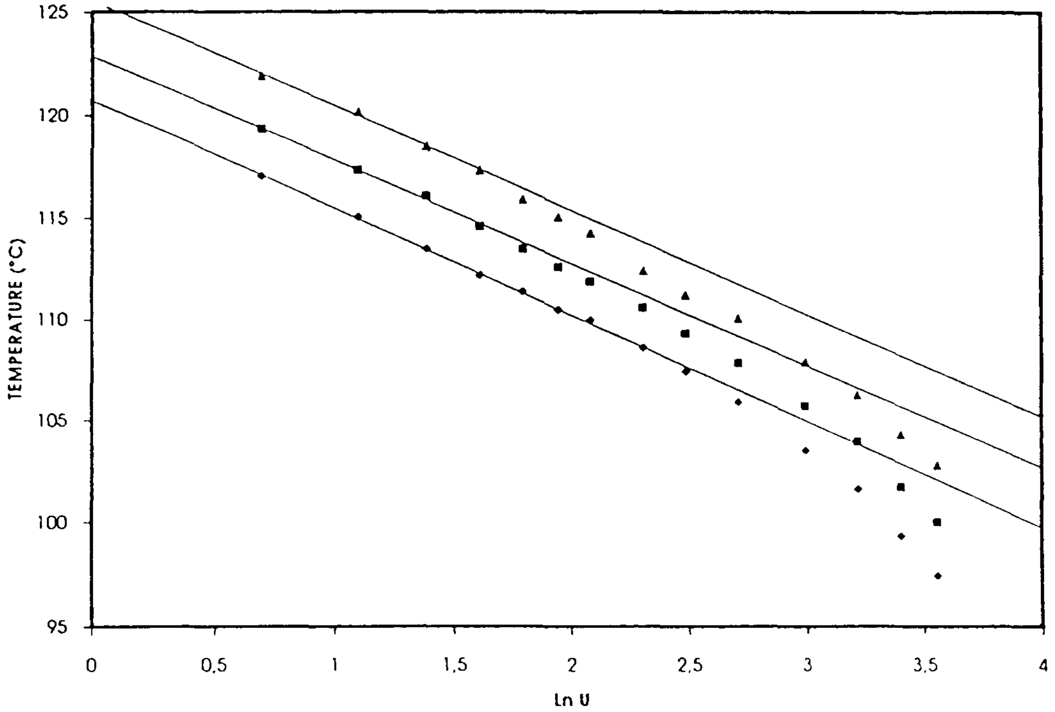

Figure 4 T_1 (▲), T_m (■), and T_2 (◆) as a function of $\ln U$ for 5% glass bead reinforced polypropylene

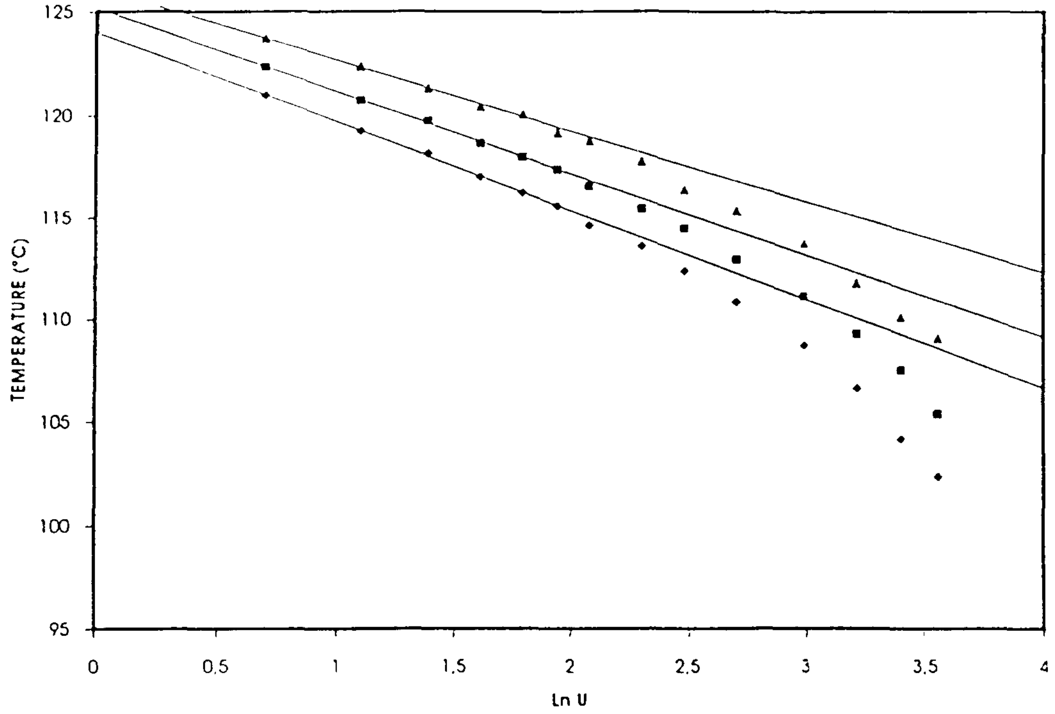

Figure 5 T_1 (▲), T_m (■), and T_2 (◆) as a function of $\ln U$ for 40% glass bead reinforced polypropylene

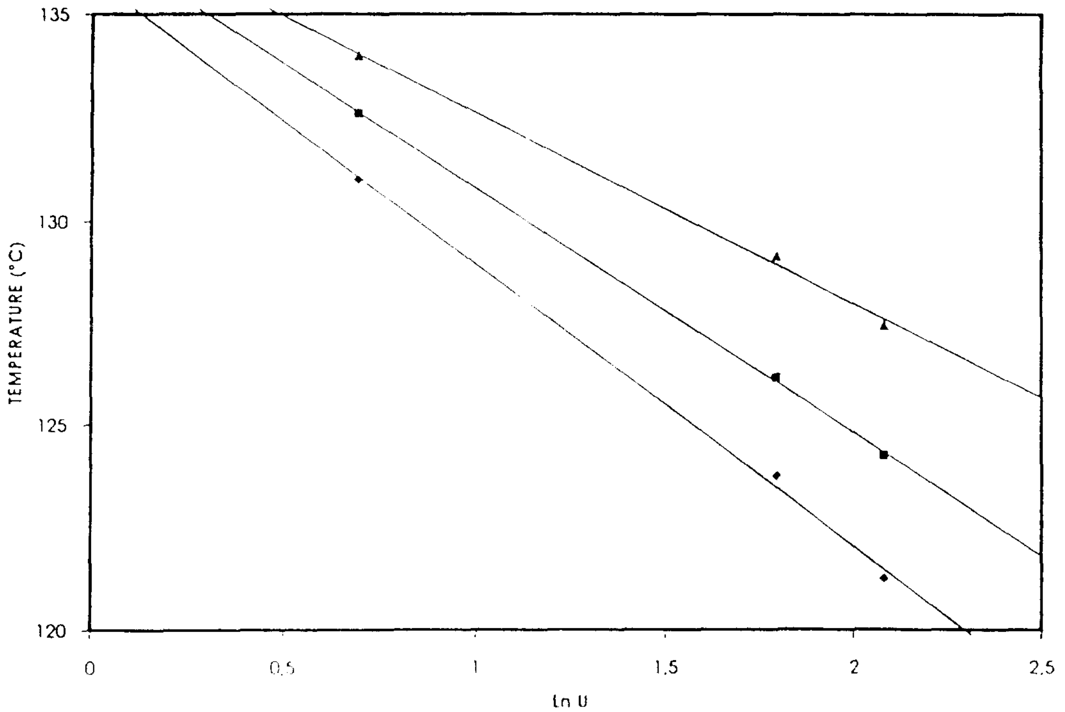

Figure 6 T_1 (▲), T_m (■), and T_2 (◆) as a function of ln U for 2% carbon black reinforced polypropylene

CONCLUSIONS

Crystallization thermograms for polypropylene cooled from the molten state were exploited using our calculus method when compared against the Ozawa theory. It appears that the determination of the maximum and of the inflexion points of the experimental exotherms for different cooling rates, is sufficient to obtain a satisfactory correlation with the theory. However, the Ozawa hypothesis cannot be eliminated, particularly when the polymer is reinforced or when there is a change in the crystallization regime. The great advantage of the calculus method is it is very simple and therefore easy to use.

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