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Polymer 44 (2003) 8071–8079
polymer
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# Evaluation of the sample temperature increase during the quiescent and shear-induced isothermal crystallization of polyethylene

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Received 26 May 2003; accepted 10 September 2003

**Abstract**

The isothermal crystallization of low-density polyethylene is analysed by differential scanning calorimetry and parallel plate rheometry. The temperature increase during the isothermal crystallization, resulting from the polymer sample's thermal resistance and the release of the heat of crystallization, is evaluated for the results obtained with both devices. The implication of this evaluation on the comparative overall crystallization kinetics is also analysed. Two different procedures for evaluating the degree of conversion to the solid phase from rheometry data are discussed. The sample temperature during isothermal DSC and rheometer experiments, these last performed over samples with different thicknesses, is evaluated and the relative crystallization kinetics compared by analysing the dependence of the reciprocal of the half of crystallization time on the estimated sample temperature at this instant. The results obtained indicate that, after performing the temperature corrections, and from an overall kinetics point of view, both procedures yield similar results.


*Keywords:* Shear; Isothermal; Crystallization

## 1. Introduction

The shear-induced crystallization is an important step during polymer processing because it determines the morphology of the final component and the resulting mechanical behaviour. Several techniques have been employed for their study [1–5].The preferred methodologies involve the use of cone and plate, parallel plate rheometers and modified Linkam hot stages. Often, the polymer melt is pre-sheared, with different shear rates and for different shearing times, at a constant temperature, above the thermodynamic melting temperature, or at the crystallization temperature. The pre-shearing effect on the crystallization kinetics is then evaluated.

The use of parallel plate rheometry for studying the crystallization kinetics involves the evaluation of the time or temperature dependence of the relative crystallinity, for isothermal or non-isothermal scans, respectively [6,7]. For a direct evaluation of the overall crystallization development during shear flow, Nagatake et al. [4] converted a rotational shear rheometer into a combined differential thermal analyser. By recording both the variation of the storage modulus (or complex viscosity) and the temperature difference between the sample and a reference, the device allowed a quantitative recording of the isothermal and non-isothermal shear induced crystallization.

Two important problems related to the use of parallel plate rheometers for analysing quantitatively, the effect of shear on the crystallization kinetics of polymers will be discussed. One is related to the rheometer temperature calibration and the average true sample temperature evaluation, which has been neglected in all works published so far on this subject. The other is related to the use of rheological measurements as a tool to follow the crystallization kinetics.

To be more precise concerning this last point, Khanna et al. [8] proposed to evaluate the degree of conversion to the solid phase from rheometry data by

$$X(t,T) = \frac{G'(t,T) - G'(0,T_m^0)}{G'(t_s,T_s) - G'(0,T_m^0)}, \quad (1)$$

where $G'(0,T_m^0)$, $G'(t,T)$ and $G'(t_s,T_s)$ are the storage modulus at time zero (or at a temperature greater than the

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doi:10.1016/j.polymer.2003.09.064

thermodynamic melting temperature, $T_m^0$), at time $t$ (or at the current crystallization temperature) and at time $t_s$ (or a temperature $T_s$) where the liquid is fully converted to the solid phase, respectively. This same relationship was used by Gauthier et al. [9] for following the crystallization of poly(ethylene terephthalate)/glass fibre samples. They concluded that it allowed the evaluation of the crystallization kinetics and the determination of nucleation and growth characteristics.

Other authors question the validity of that evaluation arguing that, by neglecting the dimensional variation of the sample during crystallization, large errors may be induced on the measurements as a result of the additional stresses on the sample [10]. Boutahar et al. proposed a methodology for following the rheological behaviour during the isothermal crystallization that involves the use of small strains and a continuous gap adjustment during the test, for allowing the elimination of longitudinal efforts induced by the dimensional variation of the sample and for enabling corrections of the moduli. According to these authors, the use of small strains ensures that the crystallization kinetics is not modified by shearing, and that it is only dependent on time and temperature. Further on, they state that for an understanding of the rheological behaviour, from a morphological point of view, a high-density nucleated polyethylene sample may be considered as a colloid of small particles (crystallites) in a liquid matrix (polymer melt).

Based on models for the variation of dynamic quantities with the filler content, Boutahar et al. proposed guidelines for determining the transformed fraction to the solid phase from rheological measurements. The distribution of stresses in each component was assumed to be represented by the Takayanagi models that require the knowledge of the dynamic moduli of both the matrix and the filler. These models yield the values of the equilibrium modulus for different values of the filler (crystallite) content. The models prediction for polyethylene was that the critical value of the filler content for the onset of yield was small ( $\cong 0$), and it was ascribed to the fact that all material was instantaneously occupied by solid nuclei. After fitting with empirical relationships the values obtained for the equilibrium modulus, and by comparing the predicted transformed fraction from DSC and rheological measurements, they proposed that, for colloid-like samples, the degree of conversion to the solid phase may accurately be evaluated (up to 0.84 of the conversion degree) from rheological measurements by

$$X(t,T) = \left( \frac{G'(t,T) - G'(0,T_m^0)}{G'(t_s,T_s)} \right)^{1/3}. \quad (2)$$

In the work of Boutahar et al. [10] and in other works [2,8,9], the results obtained from parallel rheometers for the isothermal crystallization are compared with similar DSC results. It is often found that the crystallization kinetics is comparable and even faster in a DSC than in a rheometer for the same crystallization temperatures (see for example the results shown in Fig. 10 of Ref. [10]). These results are discussible since it is questionable if the crystallization kinetics of a polymer in a rheometer submitted to small strains (0.2 [11] or 0.1 [12] at the start of crystallization and decreasing values at the end, 0.01 [11]) may be considered as quiescent. This particular point is discussed in this work, together with a careful evaluation of average true sample temperature during the isothermal crystallization, both for the DSC and the rheometer.

The other problem mentioned previously is the average true sample temperature evaluation, which requires the accounting for the effects of the sample thermal resistance and the release of the heat of crystallization. This temperature is here considered, instead of the sample's temperature profile and its change with the crystallization conditions, because its evaluation is easier. It has been assumed that those effects are unimportant, which is reasonably true for experiments carried out with thin samples in Linkam hot stages where, for the normal sample thickness ($\approx 1$ μm), area ($\approx 1$ cm$^2$) and crystallization temperatures, the maximum temperature increase is lower than 0.1 °C. For other, commonly used, experimental setups this is not the case. It was shown previously that quiescent isothermal crystallization of polymers in a DSC can only be considered as truly isothermal for high crystallization temperatures and for samples with small mass [13]. For other situations, a temperature profile develops within the sample, whose significance increases for thick samples and decreasing crystallization temperatures [14]. Similarly, in time sweep measurements of the storage modulus ($G'$), carried out in any rheological instrument, there is also a thermal lag between the temperature read by the sensor and the real sample temperature, due to the set of the thermal resistances involved and also to the release of the heat of crystallization. The sample temperature during the phase change may also be evaluated by performing a simple heat balance.

It is considered that, the sensible heat flux received by the sample equals the difference between the heat flux released within the sample due to the ongoing crystallization process, and the instrument-sensed net heat loss from the sample to the corresponding temperature sensor [14] i.e.,

$$m\bar{c}_p \frac{dT_t}{dt} = |\Delta\dot{Q}| - \frac{1}{R_s}(T_t - T_m), \quad (3)$$

where $m$ is the sample mass, $\bar{c}_p$ the specific heat capacity, $dT_t/dt$ the rate of the true sample temperature variation and $T_t$ and $T_m$ are, respectively, the true sample temperature and the temperature measured by the temperature sensor. The heat flux released within the sample is $|\Delta\dot{Q}| = m|\Delta h_c|dX/dt$, where $\Delta h_c$ is the heat of crystallization and $X(t)$ the mass fraction transformed (or relative crystallinity) at time $t$. The average true sample temperature is evaluated by numerically solving Eq. (3) using either the DSC isothermal crystallization curve ($\Delta\dot{Q}(t)$, relative to the appropriate

crystallization peak base line) or the integrated curve of the variation of the relative crystallinity, $X(t)$, with the crystallization time. This same procedure may be applied for evaluating, after adequate temperature calibration, the true sample temperature of a rheometer sample during isothermal or non-isothermal crystallizations.

## 2. Experimental

### 2.1. Samples

Experiments were carried out on a low-density polyethylene supplied by Borialis, Portugal, grade PE7324, with a density of 922 kg $m^{-3}$, and an average melt flow index of 0.55 g/10 s evaluated according to the norm ISO 1133. The values used for the thermal conductivity and heat capacity were 0.42 W $K^{-1}m^{-1}$ and 1.6 J $K^{-1}kg^{-1}$, respectively [15]. The thermodynamic melting temperature ($T_m^0$), evaluated by a Hoffman and Weeks plot, was 133.6 °C. The average heat of fusion for the DSC crystallized samples was 130 J $g^{-1}$. These samples, with around 10 mg, were prepared by controlling the thickness and area for evaluating the sample's thermal resistance. Average values of the sample's thickness and diameter were, 0.73 and 4.32 mm, respectively. The rheometer samples were prepared by a previous melting of the pellets in a hot press machine at 190 °C. A plate with around 2 mm of thickness was obtained, from which circular disks with 25 mm of diameter were cut for use in the rheometer. Attempts to analyse this material in detail with an optical microscope revealed difficult, due to the small spherulite size.

### 2.2. DSC experiments

A Perkin–Elmer DSC-7 running in standard mode was used. The temperature of the cold block was kept at 5 °C and the purge-gas flow rate at 20 $cm^3$ $min^{-1}$. Previous temperature and enthalpic calibrations were carried out with metal standards. For the isothermal crystallization experiments, the sample was held at 170 °C for 1 min, then cooled down to the desired crystallization temperature at a controlled cooling rate of 60 °C $min^{-1}$. These last experiments were performed with a temperature calibration of 0.1 °C $min^{-1}$. Further details related to the DSC data treatment procedure for these experiments may be found in Ref. [16].

### 2.3. Rheometry experiments

Rheological testing was performed in a Rheologica StressTech rheometer, with parallel plate geometry (25 mm diameter). The prepared disks were previously melted at 160 °C for more than 5 min. According to the manufacturer, the temperature accuracy of the setup used is ±0.2 °C, but the experimental results showed a poorer accuracy. A series of stress sweeps, at 1 Hz, and at several temperatures were applied to the sample. It was found that a constant stress of 580 Pa ensures linear viscoelastic behaviour in the temperature range of interest. The oscillation experiments were then performed at a constant stress of 580 Pa and frequencies of 0.1, 1 and 10 Hz, for several crystallization temperatures.

The temperature program used for shear-induced crystallization studies was as similar as possible to the one used for the DSC isothermal experiments. After a previous melting and adjustment of the appropriate experimental conditions, namely the initial gap-size and normal force, the following temperature program was used for each sample: an additional dwell time of 2 min at 160 °C (with a shearing at the same oscillation frequency of the experiment), a cooling at −20 °C $min^{-1}$ to the crystallization temperature followed by a sufficiently long dwell time at this temperature to completely record the solidification process, as detected by the stabilization of the material's storage modulus after a steep increase.

The sample temperature was measured with a grounded K-type thermocouple, from Omega, with a sheath diameter of 0.254 mm, thus enabling a response time lower than 0.3 s and a temperature accuracy of ±0.5 °C. The thermocouple was plugged into an SCB-68 connector, with proper cold junction compensation, which was then connected to a National Instruments acquisition board, PCI 6024E. A program was designed in Labview 6.1 environment for dealing with the adequate temperature compensation and for the continuous recording of the temperature signal as a function of the crystallization time. Conditions were optimised for experimental reproducibility, by performing a series of experiments, with and without the thermocouple inserted into the sample.

The values of the strain over the samples were recorded during the experiment (3% at the beginning and around 0.1% at the end), together with the values of the gap size. Both values were decreasing during the experiment thus ensuring that the sample is within the linear viscoelastic region and that, as in the work of Boutahar et al. [10], the longitudinal efforts induced by the dimensional variation of the sample are eliminated.

## 3. Results

An example of the results obtained for rheometer isothermal experiments is in Fig. 1. The results are qualitatively similar to others published in the literature. The figure shows the variation of the storage modulus with time for the nominal crystallization temperature at 113 °C and frequencies of 0.1, 1 and 10 Hz. A phenomenological analysis of the variation of the storage modulus and viscosity with the crystallization time was carried out by Yoon et al. [7]. The analysis may retain its validity for the present situation. During the apparent induction time, due to the shear effects, the entangled polymer melt chains

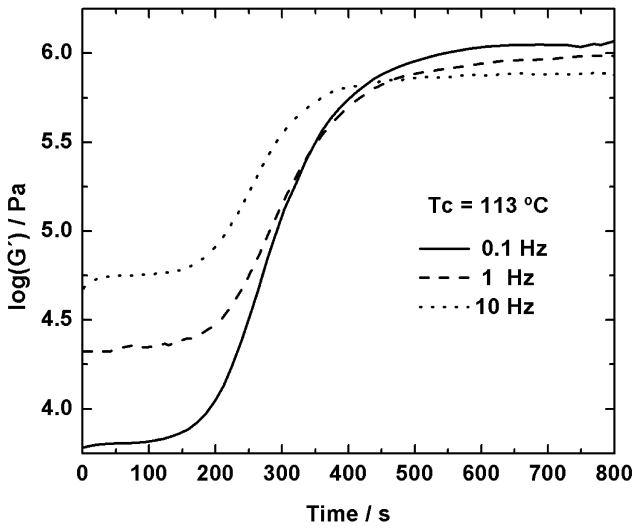


Fig. 1. Variation of log ($G'$) as a function of time for the crystallization at the nominal rheometer temperature of 113 °C. The different lines show the results obtained for the oscillation frequencies indicated.

transform into a regular aligned lattice. The increase in the modulus is due to the nucleation and progressive growth of crystallites and, finally, a similar plateau value is obtained for the three frequencies, at the end of the crystallization.

The degree of conversion to the solid phase was evaluated from results similar to those of Fig. 1 by application of Eqs. (1) and (2). Fig. 2 shows the results obtained for the isothermal crystallizations in the DSC and rheometer at the nominal crystallization temperature of 113 °C and frequencies of 0.1 and 10 Hz. The behaviour obtained is the increase of the crystallization rate with the oscillation frequencies (or shear rates). From the results of Fig. 2, it is also observable a shift to lower crystallization

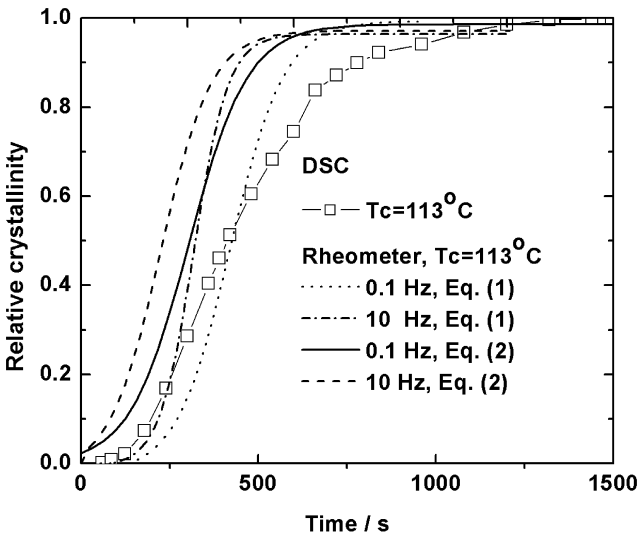


Fig. 2. Isothermal crystallization in a DSC at 113 °C and in a parallel plate rheometer at the same nominal temperature and for oscillation frequencies of 0.1 and 10 Hz. The degree of conversion to the solid phase was evaluated according to Eqs. (1) and (2). The rheometer data are presented without temperature calibration.

times of the values for the degree of conversion to the solid phase when this is evaluated according to Eq. (2), instead of Eq. (1). The consequences of using one of the above two equations, in what the crystallization kinetics is concerned, will be discussed further on in this work. The comparison of the DSC and rheometer data, for the same nominal crystallization temperature, may suggest that isothermal small angle oscillatory shear experiments have a kinetics similar to the DSC experiments at the same temperature (see for example the DSC curve and the curve obtained for $X(t)$ from Eq. (1) for 0.1 Hz).

The nominal temperatures shown in Fig. 2, for DSC and rheometer data, are not the real sample temperatures. The difference is expected to be greater for the rheometer samples, since their temperature control is poor and because those particular results were recorded without the temperature calibration.

For checking the temperature during the crystallization experiment, and to ensure that the crystallization does not occur before the starting of the isothermal period, the sample temperature was recorded with an additional thermocouple inserted into the sample, according to the procedures described in the experimental part of the work. The result, shown in Fig. 3, indicates that the nominal rheometer temperature reaches a steady isothermal process just a few seconds after the programmed temperature (the zero time was assigned to the start of the isothermal). However, the sample temperature needs more time to reach the isothermal temperature, and it stabilizes at a temperature higher than the one indicated by the rheometer temperature sensor. A similar behaviour was observed for different crystallization temperatures and shearing frequencies. The values of the nominal program temperature, the temperature measured by the external thermocouple ($T_{th}$) and the average sample gap size measured by the rheometer after

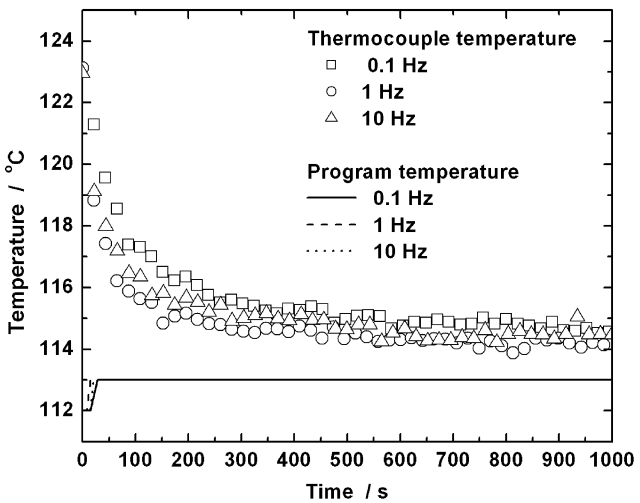


Fig. 3. The symbols show the variation of the measured sample temperature as a function of time for the programmed isothermal crystallization at 113 °C. The frequencies are indicated and the lines show the rheometer program temperature.

the solidification are in Table 1. The observed deviations (the thermocouple measurement error is ±0.5 °C and error of the nominal rheometer temperature is ±0.7 °C) suggest the need for an isothermal temperature correction. The need for this correction is also suggested by the results of Fig. 2, since it is expected that the shear deformations will accelerate the crystallization kinetics, with respect to the crystallization at the same temperature in the DSC.

For evaluating the isothermal thermal lag, common in all thermal analysis instruments, a temperature calibration of the rheometer was performed with metal standards at several scanning rates and extrapolated to zero scanning rate. A sample of the experiments performed with indium at scanning rates of 0.5 and 1 °C $min^{-1}$ is in Fig. 4. This figure shows the variation of the phase angle with temperature at the oscillation frequency of 1 Hz and a constant stress of 12 kPa. The sudden increase of the phase angle is assigned to the onset of the indium melting. From a set of experiments at several heating rates, from 0.5 to 6 °C/min, the isothermal correction evaluated at the indium melting temperature (156.6 °C) was 3.2 ± 0.7 °C, where the associated error was evaluated after a set of experiments at a scanning rate of 1 °C $min^{-1}$. At 231.9 °C, the melting temperature of tin, the isothermal correction is 6.3 ± 0.7 °C. A detailed discussion of the temperature calibration of rheometers for isothermal and non-isothermal experiments is presented in another work [17].

As a reasonable approximation, a linear variation of this correction may be assumed in the working temperature range and its value for each crystallization temperature may then be evaluated. The value obtained with this correction for different crystallization temperatures is in Table 2.

The results obtained with the rheometer were then corrected for the isothermal correction and compared with DSC results at similar crystallization temperatures. Selected results for the nominal (uncorrected) crystallization temperatures in the rheometer of 109 and 113 °C, corrected values of 110.2 and 114.4 °C, respectively, are in Fig. 5(a) and (b), respectively. Fig. 5(a), shows an unacceptable behaviour that is, for a similar crystallization temperature, the crystallization in the rheometer is starting later than the crystallization in the DSC. This behaviour can only be understandable if the average

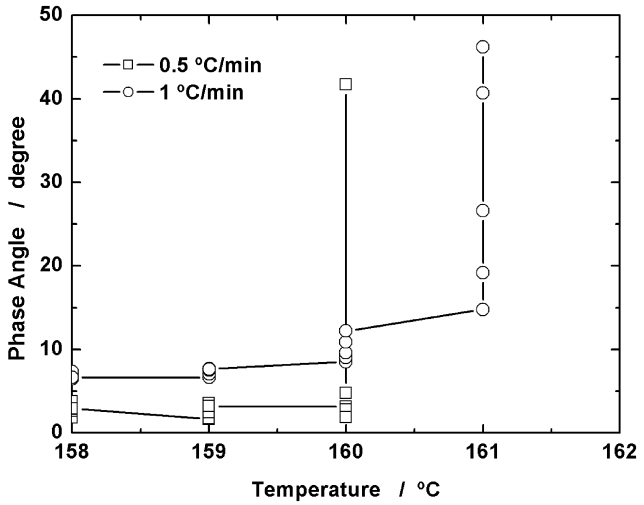


Fig. 4. Detection of the melting of indium in a parallel plate rheometer by the sudden increase of the phase angle at a frequency of 1 Hz and heating rates of 0.5 and 1 °C $min^{-1}$.

temperature of the rheometer sample is higher than that of the DSC sample. The results of Fig. 5(b) are more comprehensible. The figure shows the acceleration of the crystallization kinetics when the DSC result at 114 °C is compared with rheometer data at a similar crystallization temperature.

The meaning of these results is that, isothermal experiments performed in the rheometer are shifted from the nominal rheometer program temperature by the isothermal corrections of Table 2, which are, within the experimental error limits, in good agreement with the majority of values evaluated for $\Delta T$ in Table 1, and explains the results of Fig. 5(a) and (b).

An accurate analysis of the results obtained with both devices requires the evaluation of the average true sample temperature, both for DSC and rheometer experiments. It was shown that nominally isothermal DSC crystallization experiments may occur only for high crystallization temperatures and thin samples [13,14]. When Eq. (3) is applied to nominally isothermal experiments, the average true sample temperature during the phase change may be estimated. The result of this evaluation for several DSC experiments, at different crystallization temperatures, is in

Table 1
Isothermal crystallization in the rheometer at the temperatures and frequencies indicated. The gap size is the average value measured by the rheometer after solidification. $T_{th}$ is the temperature measured by the thermocouple inserted into the sample and $\Delta T$ is the difference between the temperatures measured by the thermocouple and rheometer

| $T_c$/°C | $\omega = 0.1$ Hz | | | $\omega = 1$ Hz | | | $\omega = 10$ Hz | | |
|---|---|---|---|---|---|---|---|---|---|
| | Gap/mm | $T_{th}$/°C | $\Delta T$/°C | Gap/mm | $T_{th}$/°C | $\Delta T$/°C | Gap/mm | $T_{th}$/°C | $\Delta T$/°C |
| 109 | 0.644 | 111.0 | 2.0 | 0.488 | 110.6 | 1.6 | 0.389 | 110.9 | 1.9 |
| 111 | 0.682 | 112.8 | 1.8 | 0.516 | 112.7 | 1.7 | 0.406 | 112.6 | 1.6 |
| 113 | 0.593 | 114.8 | 1.8 | 0.406 | 114.2 | 1.2 | 0.289 | 114.4 | 1.4 |
| 115 | 0.387 | 116.3 | 1.3 | 0.386 | 116.9 | 1.9 | 0.394 | 117.0 | 2.0 |
| 117 | 0.356 | 118.9 | 1.9 | 0.326 | 119.6 | 2.6 | 0.357 | 119.2 | 2.2 |

Table 2
Estimated isothermal correction ($\Delta T_0$) for the isothermal crystallization in the rheometer evaluated after the isothermal corrections at the indium and tin melting temperatures, and assuming a linear variation of $\Delta T_0$ in the temperature range of the work

| $T_c$/°C | 109 | 111 | 113 | 115 | 117 |
|---|---|---|---|---|---|
| $\Delta T_0$/°C | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 |

Fig. 6. Since the sample used has a relatively high thickness, it is heated both from its bottom and top. The thermal resistance value used in Eq. (3), estimated after evaluations performed according a procedure described in Ref. [14], was 60 k/W. Other values used for the sample temperature

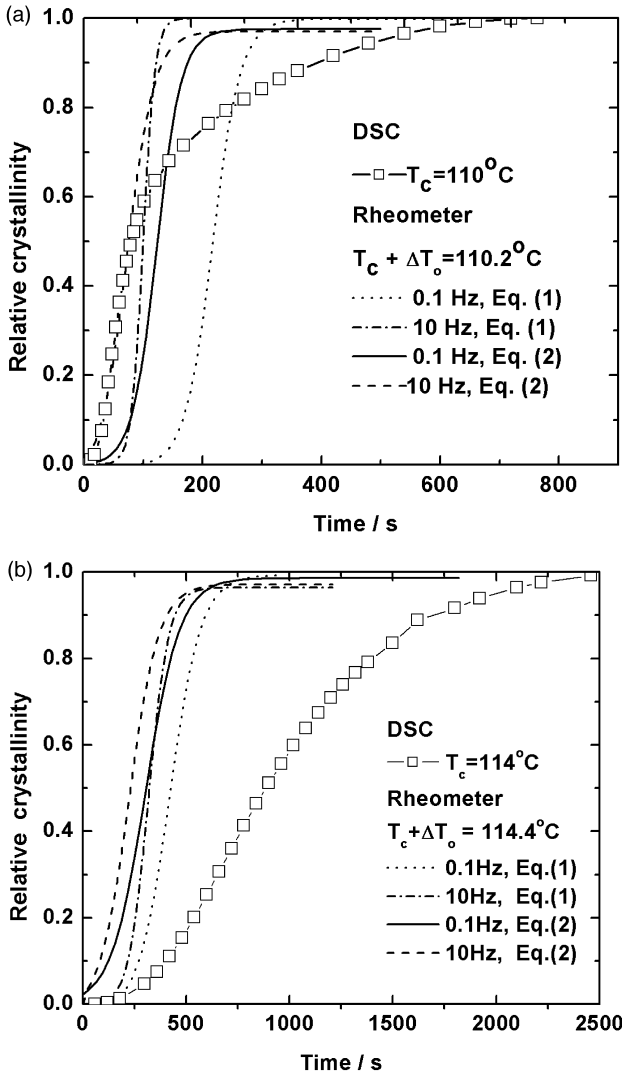


Fig. 5. Comparison of the relative crystallinity, at similar crystallization temperatures, for the isothermal crystallizations in the DSC and rheometer, with $X(t)$ evaluated from Eqs. (1) and (2). (a) Crystallization in the DSC at 110 °C and crystallizations in the rheometer at 110.2 °C (nominal, uncorrected crystallization at 109 °C). (b) Crystallization in the DSC at 114 °C and crystallizations in the rheometer at 114.4 °C (nominal, uncorrected crystallization at 113 °C). In both figures, the rheometer nominal crystallization temperatures were corrected with the isothermal corrections indicated in Table 2.

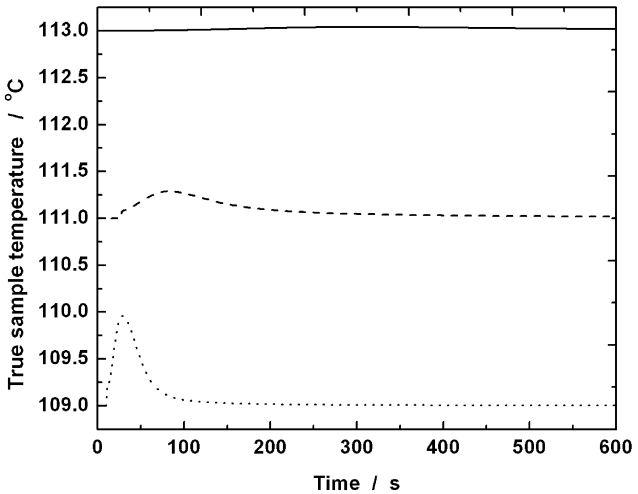


Fig. 6. Predicted true sample temperature for quiescent isothermal crystallizations in a DSC cell at 109 °C (dotted line), 111 °C (dashed line) and 113 °C (full line) ($m = 10.10$ mg, thickness = 0.73 mm, diameter = 4.32 mm).

evaluation are in the experimental part of this work. The temperature increase is small for higher crystallization temperatures where the crystallization may be considered isothermal. For lower crystallization temperatures, the temperature increase is more pronounced and it affects the definition of the average true sample temperature and the overall crystallization kinetics analysis [14].

Similar evaluations may be performed for the rheometry data. The results obtained for the nominal crystallization temperatures of 109 and 113 °C, or after the isothermal correction, 110.2 and 114.4 °C, respectively, are in Fig. 7(a) and (b) for the different frequencies tested.

The sample thermal resistance changes during the crystallization process as a result of the decreasing in the gap size. Its value was evaluated throughout the crystallization and the value of the sample weight, around 400 mg, was evaluated at the end of crystallization. The average enthalpy of fusion, evaluated by melting the samples crystallized at each temperature and frequency in the DSC, at a scanning rate of 20 °C min$^{-1}$, was 127.8 J g$^{-1}$, with a standard deviation of 3.6 J g$^{-1}$. The higher temperature increase estimated for the samples crystallized with lower shearing frequencies is only due to their higher thickness, as it may be checked from the results shown of Table 1.

Since the predicted temperature increase is a function of the degree of conversion from the liquid to the solid phases, Eqs. (1) or (2), the full symbols in Fig. 7(b) show the evaluated temperature increase when Eq. (2) is used for evaluating the degree of conversion to the solid phase. All other estimations shown in Fig. 7(a) and (b) were made with $X(t)$ evaluated from Eq. (1). The differences in the estimated values for the temperature increase with these two equations are small, within the experimental errors of the measure-

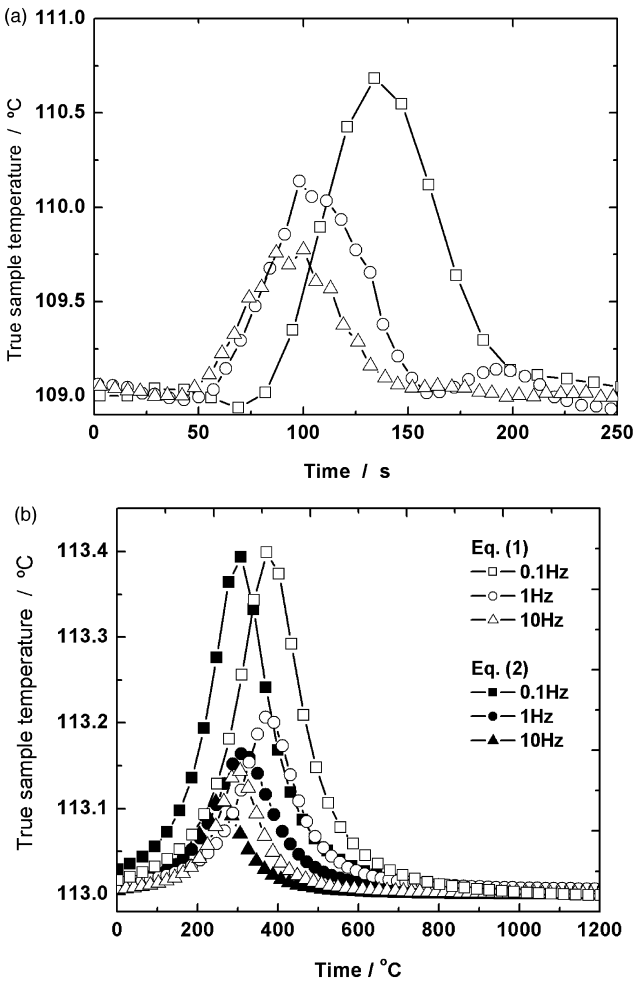


Fig. 7. Predicted temperature increase for isothermal crystallizations in the rheometer for 0.1 Hz (-□-), 1 Hz (-○-) and 10 Hz (-Δ-) at (a)109 °C (corrected 110.2 °C) and (b) 113 °C (corrected 114.4 °C). The full symbols in (b) show the true sample temperature evaluated by Eq. (3) with $X(t)$ evaluated from Eq. (2).

ments, and independent on the equation used for evaluating $X(t)$. Providing that no temperature increase due to the shear dissipation occurs, and for the oscillation frequencies used, the estimated increase due to this effect is around 0.01 °C. The evaluated temperature increase should be almost independent of the oscillation frequency, apart from any possible effect of the frequency on the kinetics itself.

The results of Figs. 6 and 7 show a variation of the sample temperature with the crystallization time. For the purpose of analysing the variation of the temperature increase with the crystallization temperature, the sample temperature at the half of crystallization time is plotted against the crystallization temperature in Fig. 8. The line with slope one shows the behaviour expected if the crystallization process was perfectly isothermal, the sample temperature being equal to the nominal program temperature. The full stars (-★-) show the evaluated temperature increase for the isothermal crystallization in the DSC at a time corresponding to half of the crystallization, and the full

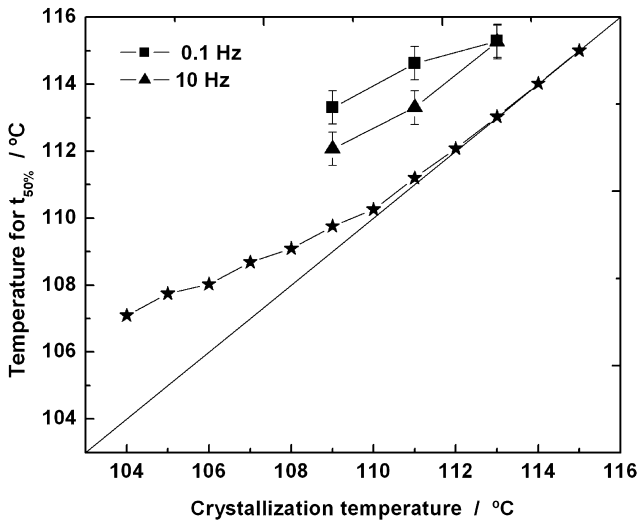


Fig. 8. Average sample temperature at a time corresponding to the half-crystallization time ($t_{50\%}$). The full stars (-★-) are the true sample temperature evaluated for the isothermal DSC experiments at $t_{50\%}$ and (■, ▲) are the values of $T(t_{50\%})$ obtained for the rheometer data after the thermal lag corrections mentioned in the text.

squares and triangles (-■-, -▲-) show the evaluated temperature increase, also at the half of crystallization time, for the samples crystallized in the rheometer at the oscillation frequencies of 0.1 and 10 Hz.

## 4. Discussion

The previous results show the importance in performing experiments with the highest possible temperature accuracy, which involves adequate temperature calibrations and true sample temperature evaluations. The comparison of isothermal DSC and rheometer data, shown in Fig. 5(a) and (b), clearly demonstrate the importance in performing temperature corrections for comparing the crystallization kinetics recorded with the two devices.

In the following, we will analyse the effect of those corrections over rheometer data, obtained at the same nominal crystallization temperature and oscillation frequency, but with samples of different thicknesses, as recorded by the measured values for the gap size. Results of these experiments for the nominal crystallization temperature of 111 °C (corrected, 112.3 °C) are in Fig. 9 for the two gap sizes indicated, with $X(t)$ evaluated from Eq. (1). Independently of the equation used for evaluating $X(t)$, Eqs. (1) or (2), the crystallization kinetics curve is shifted to lower crystallization times for thinner samples.

For finding out whether Eqs. (1) or (2) is more appropriate for evaluating the degree of conversion to the solid phase from $G'$ data, a more detailed analysis of the crystallization kinetics is required. A comparative analysis of the nucleation and growth characteristics for DSC and rheometer data may be performed if one assumes a similar temperature dependence of the spherulite growth rate. In

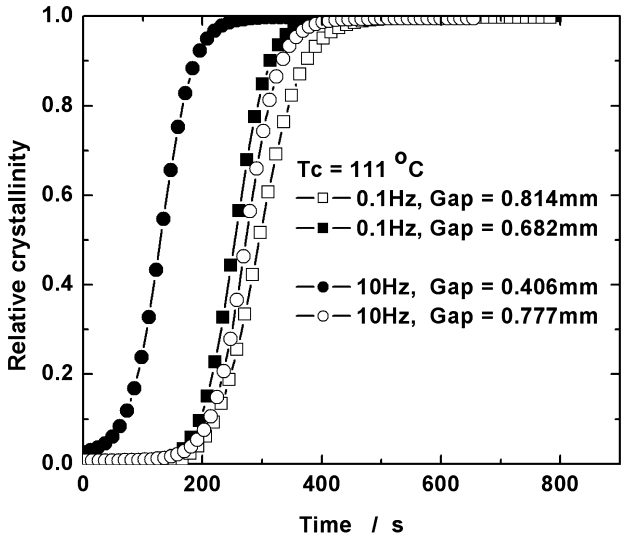


Fig. 9. Effect of the sample thickness on the crystallization kinetics at 111 °C for the oscillation frequencies of 0.1 and 10 Hz. The $X(t)$ was evaluated with Eq. (1). The indicated gap sizes were measured at the end of crystallization. The corrected crystallization temperature is 112.3 °C.

fact, a model developed by Pennings, based on the extension of the Lauritzen and Hoffman growth model for the nucleation and growth of fibrilar crystals [18], predicts that the longitudinal growth velocity of a surface nucleus, with length $L$, has approximately the following temperature dependence

$$G(T) \propto \exp\left(\frac{4L\sigma}{kT\dfrac{\Delta h_f \Delta T}{T_m^0} + \Delta G_{elastic}}\right), \quad (4)$$

where $k$ is the Boltzmann constant, $\Delta h_f$ is the enthalpy of fusion, $\sigma$ is the lateral surface energy and $\Delta G_{elastic}$ is the additional contribution of the elastic strain energy to the volumetric free energy variation, and $\Delta T$ is the supercooling (difference between the thermodynamic melting temperature and crystallization temperature). Since the above equation is applicable for a more intense melt orientation than the one existing in the present work, it is reasonable to assume that the growth rate of shear induced structures has the same temperature dependence of the quiescent crystallization.

For a quiescent instantaneous nucleation the reciprocal of the half of crystallization time is directly proportional to the growth rate, whose temperature dependence is given by the Lauritzen and Hoffman equation,

$$G(T) = G_0 \exp\left(-\frac{\Delta G_d}{k_B T}\right)\exp\left(-\frac{K_g}{T\Delta T f}\right), \quad (5)$$

where $\Delta G_d$ is the activation energy for the transport of the supercooled stem to the semicrystalline nuclei, $T$ is the absolute temperature, $K_g = cb\sigma\sigma_e T_m^0/(k_B \Delta H)$, where $c$ is 4 for regimes I and III and 2 for regime II, the other parameters having their usual meanings and $f$ is a corrective factor for the decrease of the enthalpy of fusion with the crystallization temperature. The transport term is usually assumed to be equal to $C_1C_2/(C_2 + T + T_g)$, where $C_1 = 25$ and $C_2 = 30$ K and $T_g$ is the glass transition temperature. Assuming that the semicrystalline structures developing in the samples crystallizing in the rheometer grow with the same temperature dependence as the one shown by Eq. (5), and assuming also that their thermodynamic melting temperature and glass transition temperature are not substantially affected by the shear, we may use the temperature dependence of the reciprocal of the half of crystallization time to analyse the set of results obtained for the samples crystallized at different temperatures and with different thicknesses, including those of Fig. 9.

These results are in Fig. 10(a) and (b) for the oscillation frequencies of 0.1 and 10 Hz. In these figures all the results

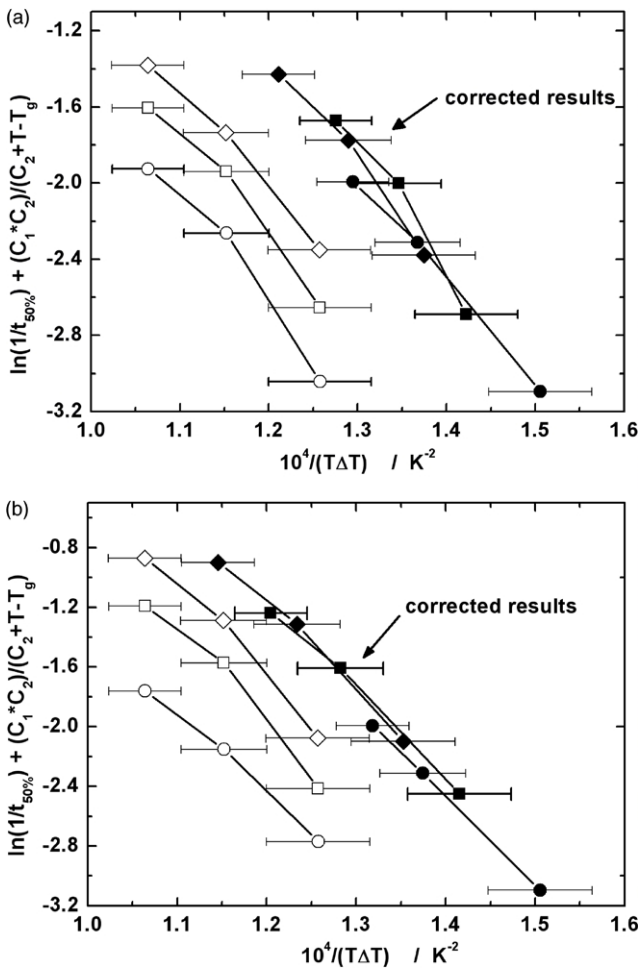


Fig. 10. Variation of the reciprocal of $\ln(1/t_{50\%})$ with $1/(T\Delta Tf)$ for a set of experiments with samples of different thicknesses. The open symbols show the results for the nominal rheometer temperature and the full symbols are for the results after the temperature corrections evaluated according to the procedures described in the text. (a) Oscillation frequency of 0.1 Hz and (b) oscillation frequency of 10 Hz. In (a) the open diamond (-◇-) is the result at 0.1 Hz for the sample with a thickness of 0.682 mm, with the $X(t)$ evaluated from Eq. (2); the corrected result is shown by (-◆-). Similarly in (b), (-◇-) is for 10 Hz, thickness = 0.406 mm, with $X(t)$ evaluated from Eq. (2). The corresponding corrected result is shown by (-◆-).

shown by open symbols (-○-, -□- and -◇-) correspond to the nominal rheometer crystallization temperature. The curves shown by squares (-□-) and diamonds (-◇-) correspond to the same result, the only difference between them is that in the first one the $X(t)$ is evaluated according to Eq. (1) while in the second it was evaluated according to Eq. (2). The full symbols represent the corrected temperatures—isothermal device correction and correction for the sample thermal resistance and release of the heat of crystallization according to Eq. (3). In both figures the error bars show the error related to the rheometer temperature measurement.

The coincidence of the results obtained demonstrates that the deviation in the results of Fig. 9 disappears after temperature corrections, which is confirmed by the set of results represented by the full circles and squares (-●-, -■-). The effect of evaluating the degree of conversion to the solid phase according to Eq. (1) or (2), which seems important in the results of Fig. 5(a) and (b), disappears completely after evaluating the true sample temperature (results shown by the full squares and diamonds (-■-, -◆-)).

## 5. Conclusions

The conclusions to be drawn form this work are the following:

1. A precise evaluation of the sample temperature during isothermal crystallization in a parallel plate rheometer is essential for comparing these results with those obtained, also during isothermal crystallizations, with a DSC. For isothermal experiments, the temperature calibration of a rheometer may be performed with standard metals and a linear variation of the isothermal correction may be assumed for evaluating the isothermal correction at the different crystallization temperatures.
2. Small angle oscillatory shear experiments at constant temperature impose to the polymer sample a different thermal and mechanical environment than quiescent experiments performed in a DSC.
3. The average sample temperature during isothermal crystallizations, both for the DSC and rheometer, may be evaluated from the available experimental data. These evaluations allow the comparison of experiments performed over samples with different thicknesses and show that apparently different procedures for evaluating the degree of conversion to the solid phase yield similar results.

## Acknowledgements

The authors acknowledge comments and criticisms made to this work by Prof J.J.C. Cruz Pinto and Dr Luzia Filipe, from Borialis, Portugal, for supplying the material used in this work. This work was carried out under financial support of the European Community fund FEDER, through the project POCTI/33061/CTM/2000 approved by the Portuguese Foundation of Science and Technology (FCT), that is also acknowledged by the grant BPD/5517/2001 assigned to WD. Zhang.

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