

Research Article

Kinetics of Phase Transformation of Indium in the Presence of Polytetrafluoroethylene: Implications for DSC Measurements on Polymers and Their Composites

Maria Raimo

Consiglio Nazionale delle Ricerche, Istituto per i Polimeri, Compositi e Biomateriali, Via Campi Flegrei 34, Pozzuoli, 80078 Naples, Italy

Correspondence should be addressed to Maria Raimo; raimo@ictp.cnr.it

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The present work focuses on the influence, at nominal constant temperatures, of an inert polymer on the crystallization kinetics of a highly conductive metal as indium (In) to show not only that the presence of a polymer allows obtaining information on the In crystallization directly from differential scanning calorimeter (DSC) curves, but also that appropriate corrections of thermal measurements on low conductivity samples are needed.

1. Introduction

Polymers show an extremely low thermal conductivity relatively to ceramic and metallic materials. Whereas computations on reaction kinetics data have been widely discussed [1], exhaustive recommendations for collecting and processing thermal data relative to very low conductivity samples, as polymers, have not been reported yet. For instance, it is accustomed to perform temperature calibration of DSC with high thermal conductivity references even for investigations on polymers, neglecting the inherent need of using calibrating reference substances with the same thermal properties of materials under investigation [2]. This constitutes a severe limit for reliability of output of melting and crystallization data and, hence, for a trustworthy comparison of results regarding polymers and their composites and blends [3]. Metals generally show sharp fusion and crystallization peaks in DSC curves as their phase transitions are relatively fast processes, whereas polymers show broad peaks mainly because of their low thermal conductivity and high heat capacity [4]; often, the melting peak of polymers appears different at different heating rates even if recrystallization and/or reorganization phenomena do not occur, just because of the nonuniform spatial melting of the whole specimen [5].

Indeed, the assumption of infinite rate propagation of heat and, consequently, of insignificant thermal gradient during heating or cooling, is invalid for polymers, especially when nonnegligible thicknesses or masses are used. Although it has been rightly observed that temperature calibration should be done with substances having the same thermal properties of the investigated sample [2], metals are still used as universal standard materials for DSC calibration even when measurements involve compounds with extremely low thermal conductivity as polymers. Owing to its narrow fusion peak and high purity, indium (In) is one of the metals used for temperature and enthalpy calibration of differential scanning calorimeters not only during heating but also during cooling [6]. Therefore, In may also be considered an ideal substance to study crystallization from melt and the influence of foreign substances on crystallization kinetics. The knowledge of the solidification kinetics of a material in the presence of a low thermal conductivity polymer is of great potential interest not only to predict the effect on the crystallization rate and hence on the processing time [7], but also to control the grain size [8] and intragrain defect density [9], which are very important when high quality crystals are required. Moreover, understanding the effect of polymers on metals crystallization allows realizing that also

interpretative analysis of thermal data concerning polymers and polymer composites may fail when the temperature of the furnace instead of that of the samples is used [5, 7, 10, 11] and, therefore, that the advice of the authors of [2] about the DSC calibration substances is not a choice but a need. For instance, it is still accustomed to compare the crystallization kinetics at a constant furnace temperature of a polymer matrix with that of much higher thermal conductivity composites, whereas for a reliable discussion of results it would be more reasonable to report the actual temperature values of samples [7]. Indeed, the necessity to account for thermal inertia and temperature gradients originated in samples during differential thermal analysis (and DSC) has been highlighted by many authors and also equations for peak corrections have been proposed [12, 13], although these rectifications are mainly ignored in the recent state of thermal analysis.

The concomitant use of a metal and a polymer is not new in DSC measurements [11]. The solid-liquid transition of In placed onto polymer sheets has been exploited for several purposes, as evaluations of thermal gradients inside polymers and thermal conductivity [14, 15]. However, previous studies address the estimation of polymer properties and did not investigate the effect of a polymer on the phase transition kinetics of metals. On the contrary, the present paper focuses on In crystallization, in order to establish the change of In phase transition kinetics in the presence of a low conductivity polymer [1, 16] and to evidence that nonconductive substances at ordinary scan rates cannot follow temperature programs in thermal equilibrium conditions with the DSC platform.

As crystallization is an exothermic process, as observed first by Gibbs the heat evolved must be carried away from the crystal growth front for advancement of solidification [17–20]. Indeed, during solidification metals may show recalescence (increase in brightness and temperature observed in solidification of undercooled metals because of latent heat release) as consequence of grains growth [21]. The rate of heat dissipation during crystallization, reflected by DSC crystallization peaks, has to be evidently linked to the crystallization rate. Le Bot and Delaunay investigated the DSC solidification of pure indium on cooling from melt and showed that crystallization starts at a temperature slightly lower than the In melting point (156.6°C), then the temperature increases at 156.6°C because of recalescence and remains constant for almost the whole crystallization, lastly decreasing to the values imposed by the settled cooling rate. The rate of heat removal during crystallization and therefore the shape of the crystallization peak depend not only on the thermal conductivities of the solidifying substance and DSC furnaces, but also on the thermal properties of substances interposed between the cooling source and the crystallizing material. The presence of a low thermal conductivity and high thermal capacity substance, like polytetrafluoroethylene (PTFE), on the bottom of the DSC pan affects the crystallization rate of In since the heat flow from In towards the DSC platform is hindered by the high resistance of the polymer sheet. Consequently, the crystallization kinetics of In, obtainable from the DSC crystallization peak, will change. As mentioned

above, this work has been undertaken to assess the mathematical dependence on time of the solidification kinetics of In when the heat pathway includes a polymer film and to draw conclusions on the influence of DSC calibrations on polymer measurements. PTFE has been chosen amongst polymers because of its excellent thermal stability. In conformity with literature, the crystallization of In has been here considered to occur *via* nucleation, growth, and cessation of growth because of grains impingement [21]. Indeed, the rate of crystallization is recognised to follow a bell-shaped trend relative to time. From mathematical considerations it can be shown that the crystallization rate of a polycrystalline substance increases rapidly before impingement not only because of nucleation but also because of growth [22], achieving the maximum soon after the start of coalescence. When the crystallization rate is maximum, the solid fraction is usually much higher than 50%. Then, because of the high length of interfaces built between crystallites, the growth is hindered in most of spatial directions and the rate of crystallization falls quickly to zero.

2. Experimental

2.1. Materials and Methods. Investigation has been carried out using a DSC 30 Mettler Toledo endowed with a TC10A/TC15A controlling unit. The apparatus was calibrated with pure indium, lead, and zinc references at various scanning rate. Reference materials for calibration were provided by Mettler Toledo; the PTFE film was supplied by Goodfellow. From a film of PTFE 0.5 and 1 mm thick, disks were cut allowing covering the whole bottom surface of the DSC pan. In all measurements, $40\ \mu\text{m}$ covered pans of aluminium were used. Smaller disks of In having a diameter of 2 mm were layered on the PTFE and submitted to the following thermal program: heating from 30 to 180°C at a scan rate $0.167^{\circ}\text{C s}^{-1}$ and fast cooling from 180 to 155°C (or 156°C) at a scan rate $-0.833^{\circ}\text{C s}^{-1}$; after 600 s at 155°C (or 156°C), the temperature was decreased down to 30°C at a rate $-0.083^{\circ}\text{C s}^{-1}$.

3. Theory

The solid-liquid transition of a pure metal occurs by heat delivery at the thermodynamic melting temperature, which remains constant until the whole solid has been transformed in liquid. If a polymer sample contained in a DSC pan was in thermal equilibrium with the platform during heating at constant rate (i.e., if heat exchange between the polymer and the DSC apparatus were immediate), by adding In into the pan the melting peak and the melting temperature of the metal should appear unchanged in the DSC curve. This is even more the case of a metal, such as In, used as a reference substance for temperature calibration. Furthermore, at the melting temperature of In the contact resistance between In and a solid polymer is negligible [14, 23] (namely, contact resistances are defined only for contact between two solids) and, because of the high thermal conductivity of In, only the polymer limits the heat exchange rate. Indeed, the DSC curve

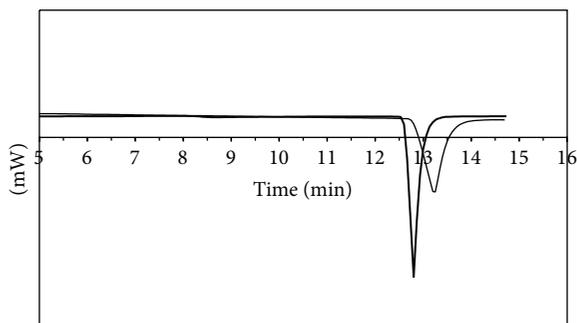


FIGURE 1: DSC melting peaks of In in absence (bold and sharp peak) and in the presence of PTFE 0.5 mm thick. The scan rate was $0.167^{\circ}\text{C s}^{-1}$.

of In laying on PTFE shows that the fusion of In apparently occurs at temperature higher than its melting temperature (156.6°C) when an underlain sheet of PTFE is also present. In Figure 1 the DSC fusion peaks of pure In, obtained by heating at $0.167^{\circ}\text{C s}^{-1}$ from 30 to 180°C , respectively, in absence and in the presence of a sheet of PTFE 0.5 mm thick, show that in the presence of PTFE a longer time is needed to melt. This demonstrates that the presence of PTFE changes the heat transfer rate between In and the DSC platform because of the low thermal conductivity and high thermal capacity of PTFE. Plotting the heat flux as function of temperature, the difference between the thermodynamic melting point of In and the transition temperature readable on the DSC curve in the presence of PTFE, may be ascribed to the thermal lag accumulated by PTFE during heating up to the fusion point of In [15]. Thermal lags may occur not only during heating [5] but also during cooling and may be evidenced even during more complex thermal programs, as in procedures for isothermal crystallization [15]. In Figure 2(a) the DSC curve of pure In, according to the thermal program described in the experimental part, is shown. This curve indicates that at the temperature of 155°C , that is, 1.6°C below the thermodynamic fusion temperature, In crystallizes rapidly. Figure 2(b) shows the DSC curve of a specimen of In placed onto a film of PTFE 0.5 mm thick and crystallized with the same procedure used in Figure 2(a). Comparing Figures 2(a) and 2(b) it emerges that in the presence of PTFE the crystallization of indium at the same furnace temperature is not immediate but requires a longer time to start and to be completed. Namely, Figure 2(a) shows that the crystallization of In starts as soon as the isothermal temperature is achieved and is completed in about 1 min, whereas Figure 2(b) shows the existence of an induction time (of about four minutes) for crystallization to start. As the temperature of the DSC platform during the two crystallization processes is the same, this difference can only be explained by assuming that the bottom layer of PTFE causes a delay in the cooling of the top layer of In. Evidently, a four-minute delay is caused by PTFE in the achievement of the sample temperature of 155°C . In addition, the overall crystallization time of In is almost twice as long as in absence of PTFE.

The isothermal crystallization peak of In in the presence of PTFE, shown in Figure 2(b), may be described by two equations. In the initial part of the liquid-solid phase transition the heat flow rate is given by

$$\frac{dQ}{dt} = h(1 - e^{-t/\tau}), \quad (1)$$

where dQ/dt is the heat flux during the phase transformation, h is a constant, and τ is the time constant proportional to the product of the thermal capacity and the thermal resistance of the system, which determine its dynamic behaviour [24]. It is well established that there is an analogy between thermal and electrical phenomena and relative quantities [14]. The electrical equivalent of formula (1) describes the charge of a capacitor in a RC circuit including also a voltage source.

In the central part of the transition, the heat flow rate still expressed by (1) is almost constant with time, whereas at the end of the transition the tailed portion of the peak (see Figure 2(b)) may be represented by the following exponential decay:

$$\frac{dQ}{dt} = h' \cdot e^{-t/\tau}. \quad (2)$$

Formula (1) is the thermal equivalent of the potential difference across the capacitor in an electrical RC circuit driven by a voltage source, whereas (2) is equivalent to the discharge of a capacitor through a resistor in a RC circuit deprived of a voltage source. Within the framework of the crystallization theory based on nucleation and growth, the exponential increase of the heat evolution rate may be related to the growth of crystalline nuclei; meanwhile other nuclei of critical dimension may be still generated. The subsequent almost constancy of the heat flow rate indicates that the equilibrium melting temperature of In has been achieved. Since nucleation needs overcooling, the constancy of the heat flow rate also indicates that the nucleation process has achieved saturation and that, therefore, only growth of grains occurs at an almost constant rate. This latter stage, which is very fast in absence of PTFE, is here prolonged as consequence of the slowdown of the heat removal through the polymer film. Finally, the exponential decay of the heat flow rate at the end of crystallization is consistent to a slowdown mainly due to impingement of crystalline grains.

In conclusion, the presence of PTFE slows down the crystallization of In and it is possible to determine not only the time needed for the overall crystallization but also the time for the completion of the nucleation process directly from DSC curves. As shown below, the same type of information can be obtained in absence of PTFE only by further processing of DSC data according to Avrami. It is worth observing that the slowdown of crystallization by using a polymer sheet may be an ingenious contrivance to achieve higher perfection of solids for particular applications, since rapid crystallization often leads to many dislocations and defects [25].

The most common approach for description of phase transformation of materials is due to Kolmogorov and Avrami, which independently derived an equation by considering the mathematical relationship between the number

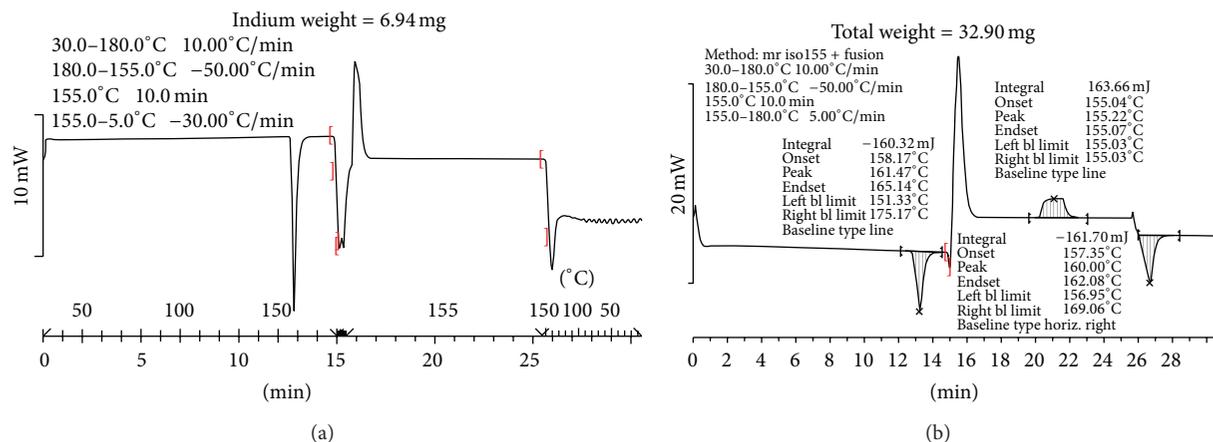


FIGURE 2: DSC curves of In, shown as an example. (a) In absence of PTFE; (b) in the presence of PTFE. An amount of c.a. 7 mg of In was first melted by heating up to 180°C s⁻¹ at a scan rate of 0.167°C s⁻¹ and then cooled up to 155°C at –0.833°C s⁻¹ and left to this temperature for 600 s. The last heating run in procedure (b) only proves that the exothermal peak is due to In crystallization.

of nuclei, supposed to be spherical, and the volume of the new growing phase under isothermal conditions, modelling nucleation as a stochastic process and growth as a deterministic phenomenon [26, 27]. Although Kolmogorov published in Russian the statistical theory on nucleation several years before Avrami, this latter is the most popular and quoted author in articles on polymers and, therefore, the phase transformation theory will be herein associated to Avrami.

The Avrami equation gives a particular solution of the more general Kolmogorov's equation and is considered to be followed by most of crystallizing materials if nucleation and linear growth rates are both constant. The application of the Avrami equation

$$\ln(1 - z(t)) = -kt^n \quad (3)$$

requires estimation of the degree of liquid-solid transformation $z(t)$ with the time t and the definition of two constants k and n , depending on the nucleation and growth of crystals, respectively. Specifically, the constant k depends on the nucleation rate whereas the so-called Avrami index n depends on the type of nucleation and the number of dimensions of the growing crystals. Actually, (3) is also valid if the nucleation rate at the zero time is infinite and then suddenly falls to zero, which means that all nuclei appear simultaneously and their number remains constant up to impingement. The nucleation constant k depends on the temperature according to an Arrhenius type dependence:

$$k = Ae^{-E_a/RT}, \quad (4)$$

where E_a is the activation energy for nucleation and R the universal gas constant.

According to the original theory, n should be an integer from 1 to 4. However, n is often not integer and even higher than four [28]. The parameter n is proportional to the crystallization rate and is obtainable from logarithmic linearization of (3) by performing isothermal DSC crystallizations of In.

The crystallinity fraction originated at a definite temperature as a function of time is generally calculated by the formula

$$z(t) = \frac{\int_0^t (dH/dt) dt}{\int_0^\infty (dH/dt) dt}, \quad (5)$$

where the numerator is the heat developed during crystallization from zero time (taken at the onset of crystallization) up to time t , whereas the denominator is the heat generated on complete crystallization. These two values are proportional to the area of the portion of the crystallization peak in the time interval $(0, t)$ and to the total area of the crystallization peak, respectively.

Equation (3) is based on postulates which often result in overestimations of the volume of the transformation product [29]. Amongst the assumptions, there is also that of uniform randomly nucleation [30]. This condition may not be respected even for rapidly quenched thin metal layers [31], meaning that practically nucleation is a process time and space dependent [28, 32] and therefore the Avrami equation can be only seemingly fitted by data collected in limited time intervals for specimens with very small thickness.

4. Results and Discussion

It is well recognised that the temperature detected by DSC is the temperature at the bottom pan [1, 12, 13, 24] and that the sample temperature depends on the thermal characteristics of the definite substance included in the pan and on the scan rate [1, 11–13, 21]. However, most of DSC manufactures advertise their efforts to reduce the thermal conductivity of the furnaces and they do not seem to take into account that the rate of the DSC response depends also on thermal conductivity of samples. High thermal conductivity substances, like metals, are also usually recommended for DSC temperature and enthalpy calibration, independently of the samples to be investigated, with the assumption that low scan rates and masses are sufficient to minimize temperature

gradients even inside low thermal conductivity samples. Even though this assumption was really applicable, it must be noted that most of the thermal procedures on polymers, like crystallization from melt, need instead fast cooling and relatively high masses of samples to overcome kinetic barriers or instrumental limits [15, 28, 33, 34]. Contrivances such as low mass and scan rates allow obtaining accurate and reproducible melting points and enthalpies even for polymers, but they are not useful for predictions of kinetic parameters relative to high masses of specimens. Indeed, the low heat propagation rate inside large specimens of a low conductivity material affects the nucleation and growth dynamics of crystallization [28]. As a consequence, different masses may show different crystallization rates even under nominally equivalent conditions. Since the crystallization rate of low thermal conductivity systems depends strongly not only on the thermal conditions but also on the mass, kinetics measurements on samples with very small thickness and mass, even if highly reproducible, are not useful to predict the true crystallization rates of industrially produced goods.

The unawareness of the above assumption may induce considering DSC performances on polymers equivalent to those on metals, causing experimental or interpretative errors [2, 5, 7, 10, 15, 34, 35] and biasing the results of kinetic methods [1, 12, 13]. In principle, the use of the true temperature should reduce errors, although it is not easy to accurately calculate or measure the true temperature of a low conductivity sample inside a DSC pan. Indeed, this measure has been up to now performed immersing in the sample thermocouples that, because of their high thermal conductivity, alter the measure itself. On the other hand, for an accurate calculation of the true temperature of a sample it is necessary to know the exact thermal conductivity, which depends on several variables [14], of that sample. To improve reliability of DSC results on polymers, it should be recognised that DSC calibrated with low conductivity reference substances would provide measurements on polymers obviously not exempted from errors but much more accurate than those performed by means of DSC calibrated with metals. The problem of using calibration substances with thermal properties different from those of the material under investigation has been discussed by Skoglund and Fransson many years ago [2]. Notwithstanding the high thermal diffusivities of calibration references have been considered by many other authors responsible for experimental errors [2, 5, 7, 10, 15] such as the temperature differences between the programmed DSC oven temperature and the actual sample temperature [2, 5, 10, 11], up to now proper measures have not been taken to improve the trustworthiness of DSC data of low conductivity substances. To prove that an appropriate temperature calibration for polymers is needed, first it is necessary to provide unequivocal evidences that equipment calibrated with metallic materials cannot provide the true temperature of low thermal conductivity samples not only during heating (as already demonstrated by authors of [2, 5, 11]) but also during cooling [2, 5, 6]. A simple way to make this evident consists in studying the crystallization behaviour of In in the presence of an inert polymer.

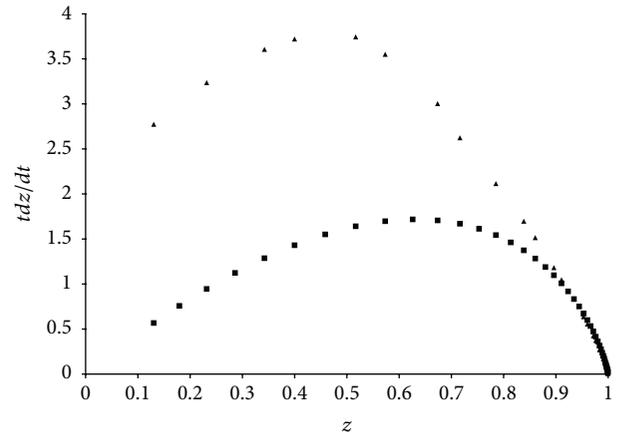


FIGURE 3: Plot of $tdz(t)/dt$ obtained, respectively, as $-n(1 - z(t))\ln(1 - z(t))$ (squares) and with the Taylor formula [34, 35] (triangles) for neat In crystallized at 155°C.

In the present work, Avrami analysis of In crystallization, in absence and in the presence of an inert film of PTFE, has been carried out at 155 and 156°C. To confirm the lack of linearity of the Avrami plot (obtained by reporting $\ln[-\ln(1 - z(t))]$ versus $\ln t$, t being the crystallization time) in the whole crystallization time, the applicability of the Avrami equation has been tested with the method of Málek and Mitsuhashi [36]. These authors have shown that the plot of $tdz(t)/dt = -n(1 - z(t))\ln(1 - z(t))$ as function of the crystallinity development $z(t)$ has a maximum point invariably at 0.632 when data fit the Avrami equation with index n . In Figure 3 both the theoretical and experimental functions $tdz(t)/dt$ are shown for In crystallization at 155°C. By comparing the two curves, it is evident that the function $tdz(t)/dt$ obtained by mathematical derivation of experimental $z(t)$ points [37] does not overlap to that calculated using $z(t)$ and the index n from Avrami analysis. The former curve shows a maximum point at a value very different from 0.632, demonstrating that the isothermal phase transformation kinetics of In cannot be described by the Avrami equation in the whole crystallization time. However, this does not exclude that sets of data may be considered to follow linear equations in limited intervals of time.

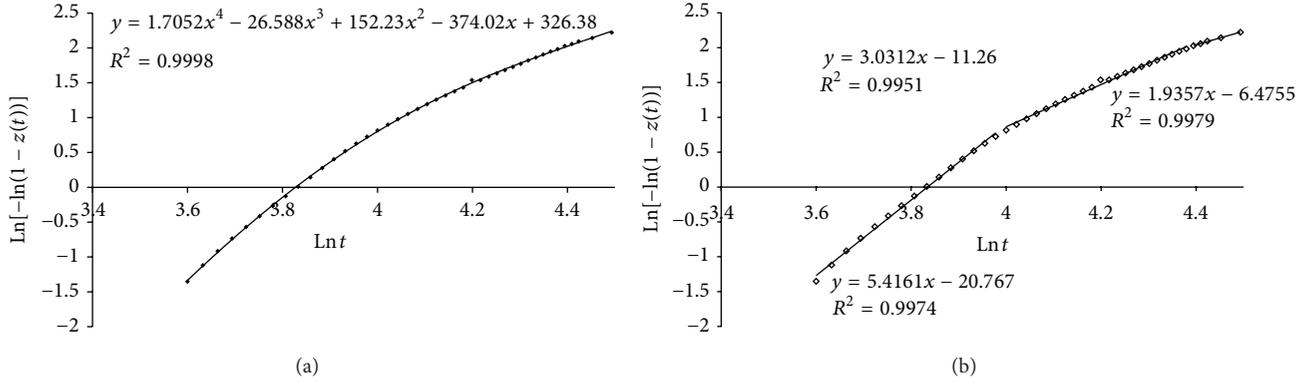
As shown in Figure 4(a), in absence of PTFE, data obtained by reporting $\ln[-\ln(1 - z(t))]$ versus $\ln t$ may be interpolated by a fourth-order polynomial expression:

$$\ln[-\ln(1 - z(t))] = c + c_1 \ln t + c_2 (\ln t)^2 + c_3 (\ln t)^3 + c_4 (\ln t)^4 \quad (6)$$

compatible with three different crystallization rates. In agreement with the three regimes observed for In crystallization by Le Bot and Delaunay [21], data show, firstly, superposition of nucleation and growth as consequence of undercooling, secondly a recalescence phenomenon which allows only growth by hindering further nucleation and, finally, a slowdown of the rate because of coalescence of grains. As a result, even if the In phase transformation cannot be described by a unique

TABLE 1: Statistical analysis of crystallization data for In at 156°C in the presence of PTFE 0.5 mm.

Type of regression	Variance	Standard error	R^2	Adjusted R^2
Logarithmic	0.1532	0.3914	0.9574	0.9564
Linear	0.1930	0.4393	0.9465	0.9452
Quadratic	0.1410	0.3755	0.9617	0.9598
Cubic	0.0190	0.1378	0.9950	0.9946
Quartic	0.0060	0.0771	0.9985	0.9983
Fifth-order polynomial	0.0027	0.0521	0.9993	0.9992

FIGURE 4: Plot of $\ln[-\ln(1 - z(t))]$ against $\ln t$ for In isothermally crystallized at 156°C. (a) Polynomial regression. (b) Linear interpolations in limited ranges of $\ln t$.

Avrami equation (likely because of the invalidity, during the whole crystallization, of the assumption of uniform nucleation with respect to both space and time) data may be considered to fit the Avrami equation in three limited time intervals. Hence interpolations of data according to three regression lines, shown in Figure 4(b), allow differentiating three crystallization regimes and appreciating the duration of each regime. From Figure 4(b) it can be deduced that nucleation of In at 156°C lasts about 53 s ($\ln 53 \cong 4$) and that during this period also growth occurs as the slope of the first line in the Avrami plot is higher than 4. In the remaining two crystallization periods the increase of the solid phase is only ascribable to the mechanisms of pure growth ($\cong 26$ s) and impingement ($\cong 8$ s), without the development of new nuclei. Indeed, if the mechanisms of nucleation and growth were overlapped for the whole crystallization time, under the hypotheses of constant nucleation and linear growth rates, data would be laid out according to a unique Avrami-type equation with n being equal to 4, but this condition is not even valid for the regression line associated to the initial part of crystallization. Instead, the line associated to the second crystallization regime has a slope of 3.0, consistent with a constant three-dimensional growth of the solid phase in absence of new nucleation. The slope of the third line is even less than 3 because collisions oblige grains to growth by filling up the decreasing empty space. Furthermore, it is possible to calculate the linear growth rate by microscopic analysis of surfaces according to a recently reported method [37]. This method is based on the identification in a solid of grains that have been growing from the onset to the end of

the crystallization continuously, at least in a few particular radial directions. Briefly, the estimation of the maximum radial size of grains of crystallized In allows the calculation of the linear growth rate G by dividing such a size for the overall crystallization time.

In the presence of PTFE a polynomial dependence is also found:

$$\ln[-\ln(1 - z(t))] = c' + c'_1 x + c'_2 x^2 + c'_3 x^3 + c'_4 x^4 \quad (7)$$

with $x = \ln t$

meaning that Avrami-type regimes may be still maintained, although the crystallization rates and the time extent of the regimes may change. In Table 1 statistical parameters are reported for comparison of several type of interpolating functions, justifying the higher accuracy of polynomial interpolations, of degree higher than one, also in the presence of PTFE.

For instance, in Figures 5 and 6 the Avrami plots of In at the temperature of 156°C in the presence of PTFE 0.5 mm thick and PTFE 1 mm thick are, respectively, shown. These plots demonstrate that the coefficients of (6) vary in the presence of PTFE and that the crystallization kinetics of In is altered in the presence of a polymer because of the change of the heat removal rate during phase transformation. The coefficients of the equations describing the kinetics of In in the presence of PTFE 0.5 and 1 mm thick are close since the crystallinity development is different from that of neat In but appears similar in the two current cases. Although a linear interpolation is not possible in the early stage of

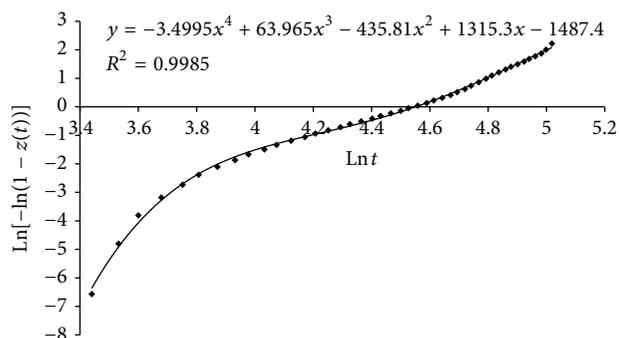


FIGURE 5: Plot of $\ln[-\ln(1-z(t))]$ against $\ln t$ for In laying on a PTFE layer 0.5 mm thick and nominally crystallized at 156°C.

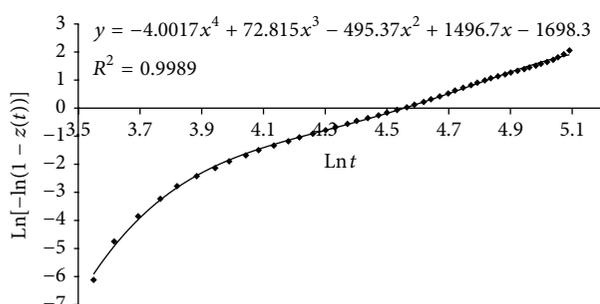


FIGURE 6: Plot of $\ln[-\ln(1-z(t))]$ against $\ln t$ for In laying on PTFE 1 mm thick and nominally crystallized at 156°C.

crystallization, two distinct regimes can be recognised in Figures 5 and 6. Indeed, if a constant growth rate is assumed for each PTFE thickness, the Avrami plots indicates that the nucleation process is globally slower in the presence of PTFE and that its rate decreases with time. Hence, meanwhile In crystallization in absence of PTFE occurs mainly with an increasing growth rate in the first and second regimes, under thermal transport constrictions the crystallization rate of In increases only in the first regime where superposition of nucleation (with a nucleation rate decreasing up to zero) and growth occurs. Later, the crystallization growth rate remains constant because the heat accumulation in the remaining liquid portions of In slows down growth of grains and hinders further nucleation.

It is worth noting that to compare the overall time required for the nucleation completion during In crystallization in absence and in the presence of PTFE, it is necessary to take into account also the induction times, which are readable directly from the DSC crystallization curves. Indeed, the zero time in the Avrami analysis is assumed as the instant at which effects of crystallization become to be detected. It is evident that in the presence of PTFE the onset of crystallization does not coincide with the time at which the platform temperature achieves the prefixed isothermal value as a longer time is needed to cool the content of the DSC pan. If the induction time is ignored, the comparison of Figures 4, 5, and 6 could lead to the incorrect conclusion that the presence of PTFE does not affect the process of nucleation of In.

Since the cooling and, therefore, the crystallization of In is delayed in the presence of PTFE for a merely thermal effect, it is evident that also the cooling of a polymer alone in a DSC device entails a thermal lag which is proportional to the thermal excursion. Thermal lags must also affect the shape and the area of DSC peaks and, therefore, the enthalpy evaluations.

The awareness of the temperature difference between the DSC platform and low conductivity specimens is necessary not only to compare correctly kinetic and thermodynamic parameters of materials, but also to consider new explanations for thermal phenomena typical of substances as polymers. For instances, authors of [5] studied the melting behaviour of polyethylene samples at different scanning rates and masses, showing that the differences in melting temperature distributions were entirely due to thermal inertia of the investigated polymer samples [5]. Similarly, double fusion peaks often observed in DSC curves of polymers could be due to the early fusion of the portion of specimens in contact to the platform followed by the late fusion of the interior. In other words, double fusion peaks may reflect a temporary slowdown of the propagation rate of the liquid front (a phenomenon concerning melting somehow “equivalent” to recalescence during crystallization) due to the powerlessness of the DSC settled procedures to provide shortly the whole heat of fusion to samples with low thermal conductivity and high thermal capacity [12, 13]. Therefore, it is advisable to observe the changes of the shape of the fusion peak with the progressive reduction of the sample mass [1] before to draw any conclusion on the nature of multiple peaks. Only if very thin films continue to show a fusion double peak even at high heating rate, a stepwise fusion of the sample can be excluded and other explanations for this effect may be considered.

5. Conclusion

It has been shown that the DSC curve of In crystallization in the presence of PTFE provides direct information on the crystallization process and, contemporaneously, that the temperature of a layer of a polymer film does not coincide with the temperature detected by DSC during either heating and cooling. Therefore it is explicitly advised that all kinds of DSC kinetic evaluations involving polymers be obtained using the actual sample temperature variation rather than the DSC reference temperature. This conclusion entails the necessity of effective methods to determine the true temperature of polymer samples during DSC analysis. More conveniently, the temperature calibration of DSC equipment could be performed by using low thermal conductivity reference materials when accurate measurements on polymers are needed.

This enquiry also evidences that even crystallization kinetics of high thermal conductivity substances like metals should be performed according to the International Confederation for Thermal Analysis and Calorimetry (ICTAC) kinetics Committee recommendations [1] when low thermal conductivity substances are present. It is necessary the use of the true temperature instead of the reference temperature also to perform computations on DSC data regarding low thermal conductivity samples.

Moreover, it has been assessed that the phase transition kinetics of In do not follow the Avrami equation in the whole crystallization time because of invalidity of the assumptions of uniform spatial and temporal nucleation. The polynomial dependence on $\ln t$ of the function $\ln[-\ln(1 - z(t))]$ found for In indicates that data may be considered to follow the Avrami equation in three separate time intervals which represent three crystallization regimes. Indeed, during the first crystallization regime the crystallization rate increases owing to the overlapping processes of nucleation and growth, then the number of grains remains unchanged and, in the presence of PTFE, the linear growth rate of grains is likely to be decreased by the slowing down in heat transfer so that the overall crystallization rate remains almost constant. Finally, the rate of solid-liquid conversion decreases because of grains coalescence. It has been shown that, because of the different thermal properties of polymers relatively to metals, there is a slowdown of the phase transition of In in the presence of PTFE. As a consequence, there is also a change of the coefficients, relatively to neat In, of the polynomial equation describing the In crystallization. The change of the crystallization kinetics can be exploited to control the morphology and, hence, the properties of materials. For example, the slowdown of the crystallization of a material caused by the presence of a low thermal conductivity polymer could be utilized to obtain highly defect-free crystals of large dimensions for advanced applications.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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