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Methodology to get the isothermal and non-isothermal bulk crystallization kinetics of iso-polypropylene by the use of a hot stage and its comparison with data obtained by light polarized optical microscopy from film crystallization.

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ABSTRACT

This work is focused on the teaching improvement of polymer phase transformation at the laboratory for under and post-graduate students. It defines a method to determine the bulk and another one to determine the film crystallization behavior respectively of iso-polypropylene under non-isothermal and isothermal conditions by the use of a hot stage Linkam DSC600 and the polarized light optical microscopy technique (PLOM); in such a manner that enables the comparison of both results. The objective is to provide a simpler, rougher, lower cost, easier to use instrument than DSC equipment, in order to enable students to get hands-on experience. This work determines the repeatability of the method that determines the bulk crystallization behavior by the parameters *n* of Avrami model and $t_{1/2}$, compares them to the ones determined from film crystallization and confirms the parameter *n* with the type of nucleation observed through the microscopy. The variability obtained in parameters *n* and $t_{1/2}$ and the fact that both methods got the same results: the i-PP has a thermal nucleation with 3 dimensions crystal growth under non-isothermal conditions and an athermal nucleation with 2 dimensions crystal growth under isothermal conditions; indicates that the method for bulk is reliable.

Keywords: Differential scanning calorimetry; Polarized light optical microscopy; hot stage; Non-isothermal crystallization kinetics; Isothermal crystallization kinetics

1. INTRODUCTION

One of the techniques to analyze the crystallization kinetics of a polymer by thermal changes is the differential scanning calorimetry (DSC). This technique uses an instrument with the same name and with the following basic characteristics:

- It contains two temperature sensors one for the reference and the other for the sample.
- The cell or heating chamber is thermally isolated as well as the cell lid.
- The instrument controls the temperature of the reference depending on what was programed by the operator
- The heat power absorbed by the sample is calculated by the temperature difference between the reference and the sample by the equation 1

$$\dot{Q} = \frac{\Delta T}{R} \qquad (1)$$

where $\dot{Q}$ is the heat power absorbed by the sample, ΔT is the temperature difference between the reference and the sample and R is the thermal resistance of the heat transfer bridge between the reference and the sample (Joseph D Menczel et al., 2009).

The main differences of the hot stage Linkam DSC600 used in this work vs. the DSC instrument are the following among many others (see Fig. 1):

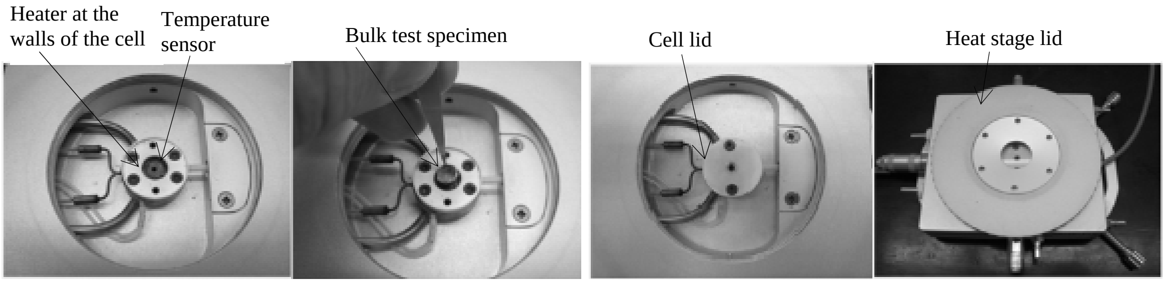


Fig. 1 Hot stage Linkam DSC600

1. It contains only one temperature sensor, so the power absorbed by the sample can't be calculated by the equation 1. Instead, the hot stage reports the heat power supplied to the heater in DSCCounts units which are based on the heater consumed electrical power.
2. The cell is not thermally isolated, so the registered thermal data includes the heat power dissipated to the ambient (which is not constant and changes with cell temperature) among the heat power of interest which is the one absorbed by the sample due to the specific heat (c_p) and phase transformation.

These two differences makes difficult to isolate the heat power released by the sample due to the exothermic process of crystallization, however the method developed in this work enables to do so.

Because DSC instrument is more expensive, fragile and complicate to use compared to the Linkam DSC600, most laboratories allow the use of the DSC instrument only to restricted trained technicians. On the other hand, Linkam DSC600 opens the chance to get hands-on experience by having less restriction to most people interested in studying crystallization process of polymers.

2. EXPERIMENTAL

The polymer used for this work is a transparent iso-polypropylene which main application is packaging. The thickness of the polymer is 0.03 mm; forward this polymer will be referred to as sample-PP.

2.1. SPECIMEN PREPARATION FOR BULK TESTS

The items used for the preparation of the specimen were a hot plate and a blade; the sequence to prepare it, is illustrated in Fig. 2. From left to right, the first photo shows how the blade is used as a squeegee to stencil the melted polymer over the hot plate in order to get a thicker film which is shown in the second photo. This thicker film allows the cut of small sheets that fit into the pan of 6 mm diameter to fill it up to the full capacity of 2 mm height, as illustrated in the third photo in Fig. 2.

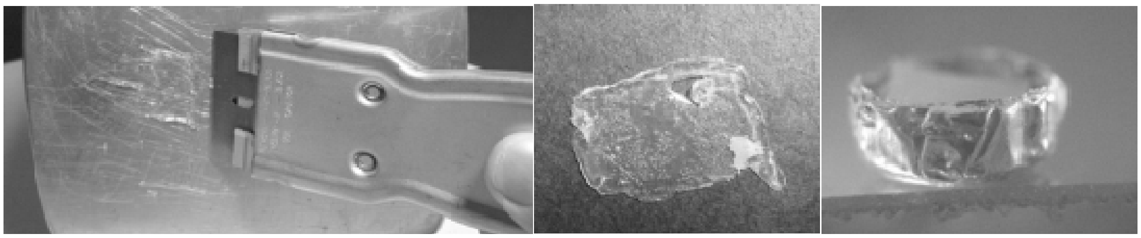


Fig. 2 Specimen preparation sequence

2.2. SPECIMEN PREPARATION FOR FILM TESTS

For the specimen preparation two options are available:

a) Specimen with crystallization in just one level as shown in Fig. 3

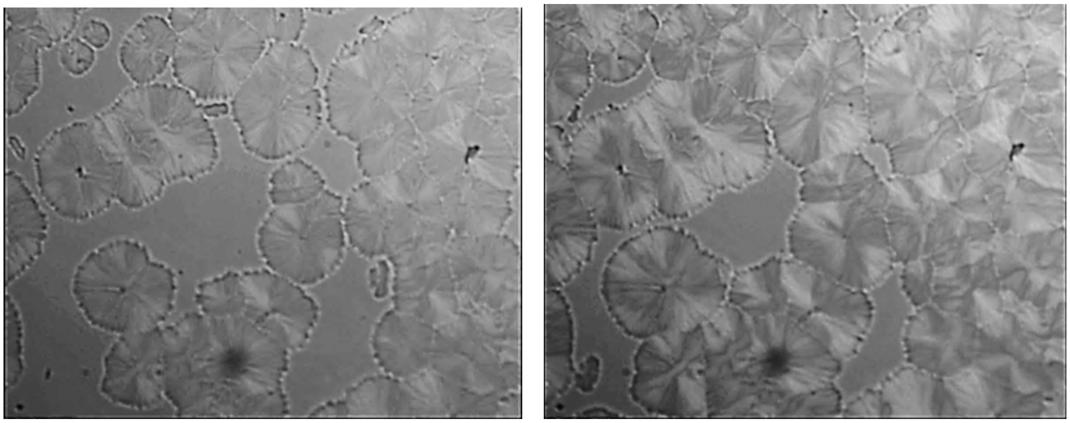


Fig. 3 Specimen with crystallization in one level (20x)

b) Specimen with crystallization in several levels depicted in Fig. 4

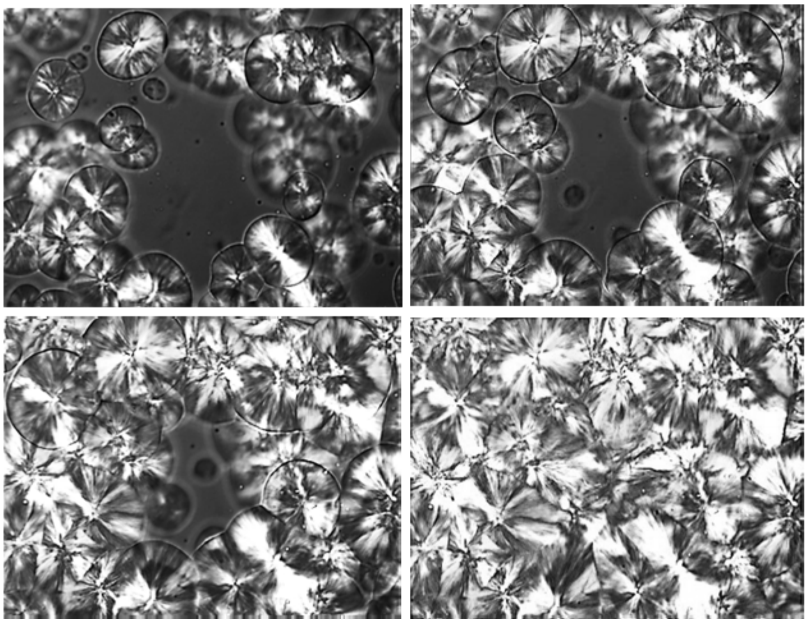


Fig. 4 Specimen with crystallization in several levels (20x)

Unlike the bibliography (B. Rojas de Gáscue et al., 2000), (Vittorina Balsamo et al., 2004), (Liliana B. Nohara et al., 2006), (K. E. Strawhecker et al., 2003), (Elda B. Hermida et al., 2004) in which the crystallization used is a), the chosen one for this work was b) because this type of crystallization is similar to bulk.

The specimen was prepared by cutting, from the original sample-PP, a square piece 5 x 5 mm and positioning it between two microscopy glass slides. The glass slides used were Corning brand with dimensions 22 x 22 mm and with a thickness rage of 0.196 – 0.201 mm.

The film specimen was placed over the cell lid of the hot stage unlike the bulk specimen which was placed over the temperature sensor inside the cell as shown before in Fig. 1 page 2.

2.3. BULK TESTS TEMPERATURE PROFILE AND PROCEDURE

All tests were carried out in the presence of atmospheric air.

The heating, for the non-isothermal and isothermal crystallization process specimens, was at a heating rate of 10 °C/min as follows:

1.- They were first heated up to 50 °C and hold for 5 min.
2.- After, they were heated up to 240 °C and hold for 5 min.

This heating makes sure that the sample-PP melts completely and all thermo-mechanical history is erased. The approximated melting point for the sample-PP is 166 °C which is taken from the maximum temperature at the endothermic melting process.

The cooling, for the non-isothermal crystallization process specimens, was carried out, right after the two heating steps mentioned before, at 5 different cooling rates: 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 40 °C/min.

Because there is no cooling system, the cooling depends on the temperature difference between the specimen and the laboratory ambient temperature which is 24 ±1°C. For this reason, the test with cooling rate of 15 °C/min lost the cooling rate control right after the crystallization process, the one with cooling rate of 20 °C/min lost it after 50% of relative crystallinity and the last one, with cooling rate of 40 °C, before the beginning of the crystallization process.

The cooling, for the isothermal crystallization process specimens, was also carried out right after the two heating steps mentioned before as follows:

1.- They were cooled off at a fastest cooling rate possible by dialing on the hot stage instrument software a maximum set point of 130 °C/min.
2.- After, they were hold at 4 different crystallization temperatures: 115 °C, 120°C, 125°C and 130°C for a time longer than the crystallization process duration.

Because there is no cooling system, the maximum cooling speed average reached for each crystallization temperature was in range of: 37 °C/min for the crystallization temperature of 115 °C and 41.5 °C/min for the crystallization temperature of 130 °C.

For the non-isothermal crystallization tests a different specimen was used for each cooling rate but the same specimen was run 4 times, under the same temperature profile, for each cooling rate in order to check the variation of the method. The same was made for isothermal crystallization tests but the same specimen was run 3 times instead of 4.

2.4. FILM TESTS TEMPERATURE PROFILE AND PROCEDURE

Because the film specimen is placed on the cell lid and not on the temperature sensor inside the cell, the temperatures for the profile are referred as set points not actually as the temperature of the specimen.

The temperature profiles for the film tests with non-isothermal and isothermal crystallization were the same as for bulk tests. However, several other crystallization temperature set points were run for the film tests with isothermal conditions in order to see which one has a crystallization kinetics that best fits the one obtained in bulk tests: 115 °C, 120 °C, 125 °C, 130 °C, 135 °C, 145 °C, 150 °C, 155 °C and 160 °C. The fit is checked by overlapping film and bulk kinetics charts at the point of 50% of relative cristallinity. A sequence of photos was taken every second during the film crystallization process.

3. METHOD FOR BULK AND FILM TESTS

3.1. BULK TEST METHOD

This work proposes:

- For non-isothermal and isothermal tests:
  - a graphic method to determine the base-line
  - an iteration process in matlab to adjust the Avrami parameters *n* and *k* to the real crystallization behavior data.

- For isothermal tests only, a method to deal with lost information at the beginning of the crystallization.

The above mentioned is pointed out by bold, underlined cap letters in the flow chart of Fig. 5.

From the flow chart of Fig. 5:

- Equation in subsection 3.2 describes the evolution of the entalphy during crystallization which represents the phase change (Pakin Thanomkiat et al., 2004) (Xinyuan Zhu et al, 2001).
- The equations in subsection 4.1 describes the Avrami model (Avrami, 1976). The Avrami model describes primary crystallization only so, the assumption that primary crystallization usually ends around 50% of relative crystallization is taken (Arnaldo T. Lorenzo et al., 2007).
- The check up of the use of Avrami model in non-isothermal tests was made by checking the error between the activation energy calculated by Arrhenius equation (Cebe P. et al., 1986) and Kissinger equation refered to the latter. This procedure has been used by other research works (Xinyuan Zhu et al., 2001), (Jian Li et al., 2001), (Hong-siang Teng et al., 2002).

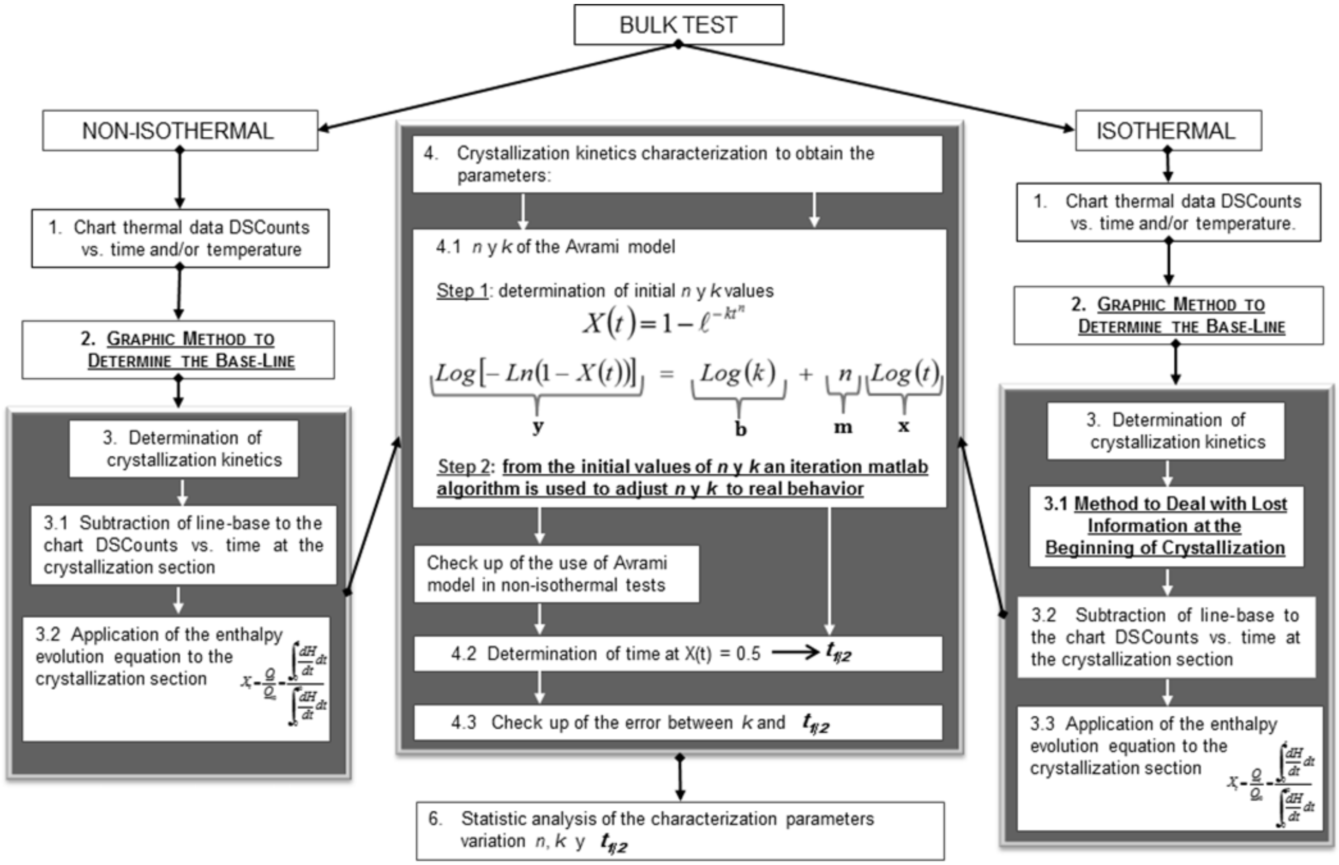


Fig. 5 Flow chart followed by this work

3.2. FILM TEST METHOD

This work proposes a method to determine the crystallization kinetics from film samples with several levels of crystallization as mentioned before and depicted in Fig. 4. The sequence of photos of the film crystallization process was obtained by polarized light optical microscopy (MOLP) using an Olympus BX51 microscopy and a QImaging Micro Publisher 3.3 RTV camera. The photo in which the crystallization process starts is identified by looking for tiny shadows where nucleation starts (initial photo) and the photo in which it finishes is identified by the observation of no further changes between photos (final photo). The software QCapture Pro 6.0 was used to process and analyze the optical data of the initial, final and all photos in between the crystallization process sequence of photos. All photos were passed throw a horizontal filter. After that, the statistical mean for the optical parameters red, blue and green of each photo was determined by the software. An average based on the addition of red, blue and green statistical mean values was calculated for each photo (this parameter is referred to as "average RBG"). The kinetics chart was determined based on the average RBG of the initial photo, the final photo and the photo at each time; the relation of these optical data to determine the relative cristallinity over time is defined by the equation 2.

$$X(t) = \frac{AverageRBG_{\text{photo t=t}} - AverageRBG_{\text{initial photo}}}{AverageRBG_{\text{final photo}} - AverageRBG_{\text{initial photo}}} \qquad (2)$$

4. RESULTS

4.1. NON-ISOTHERMAL CRYSTALLIZATION

The Fig. 6 shows the bulk non-isothermal crystallization kinetics obtained from the second of four times each specimen was run.

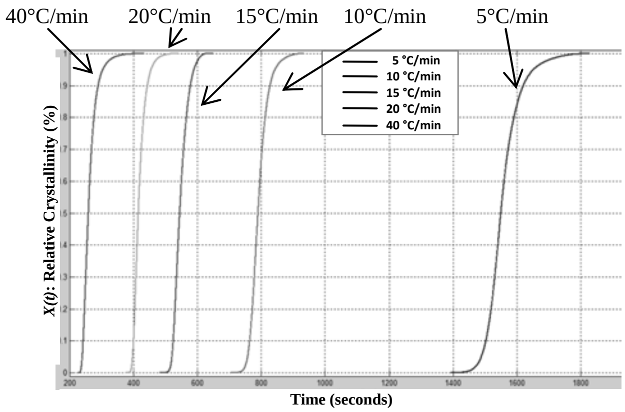


Fig. 6 Bulk non-isothermal crystallization kinetics at 5, 10, 15, 20 and 40 °C/min

The value of the parameter *n* around 4 (see Table 1) indicates a thermal nucleation with three dimensions crystal growth for non-isothermal crystallization process. The data from the test with cooling rate of 40 °C/min was eliminated as there was no control of the cooling rate all along the crystallization process.

Table 1 Avrami parameters and $t_{1/2}$ for bulk non-isothermal crystallization process at 5, 10, 15 and 20 °C/min

Cooling rate (°C/min)	Test Repetition	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)	Cooling rate (°C/min)	Test Repetition	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)
5	Initial Test	3.404	1.70843 e-08	161.4	15	Initial Test	4.407	0.958438 e-08	61.11
	1 rst time	3.417	1.80740 e-08	156.1		1 rst time	4.361	1.02535 e-08	62.53
	2 nd time	3.601	1.31854 e-08	135.7		2 nd time	4.242	3.30631 e-08	53.61
	3 rd time	3.512	1.45373 e-08	149.9		3 rd time	3.977	1.39081 e-07	48.75
10	Initial Test	3.954	1.39562 e-08	86.35	20	Initial Test	4.014	2.34251 e-07	41.33
	1 rst time	3.993	1.30981 e-08	83.87		1 rst time	3.833	5.46613 e-07	39.53
	2 nd time	4.120	1.24694 e-08	75.13		2 nd time	3.773	7.87283 e-07	38.04
	3 rd time	4.072	1.34154 e-08	76.87		3 rd time	4.002	2.79090 e-07	40.07

The Fig. 7 contains the intervals chart at a confidence of 95 % for parameters *n* and $t_{1/2}$. According to the intervals chart, the mean value of *n* seems to have no significant difference for cooling speeds of 10, 15 and 20 °C/min, however for cooling speed of 5 °C/min the mean value of *n* has a small decrement compared to the others; this might be because at a low cooling speed the thermal nucleation gets minimized. The mean value of $t_{1/2}$ decreases significantly for each cooling rate as the cooling speed increases.

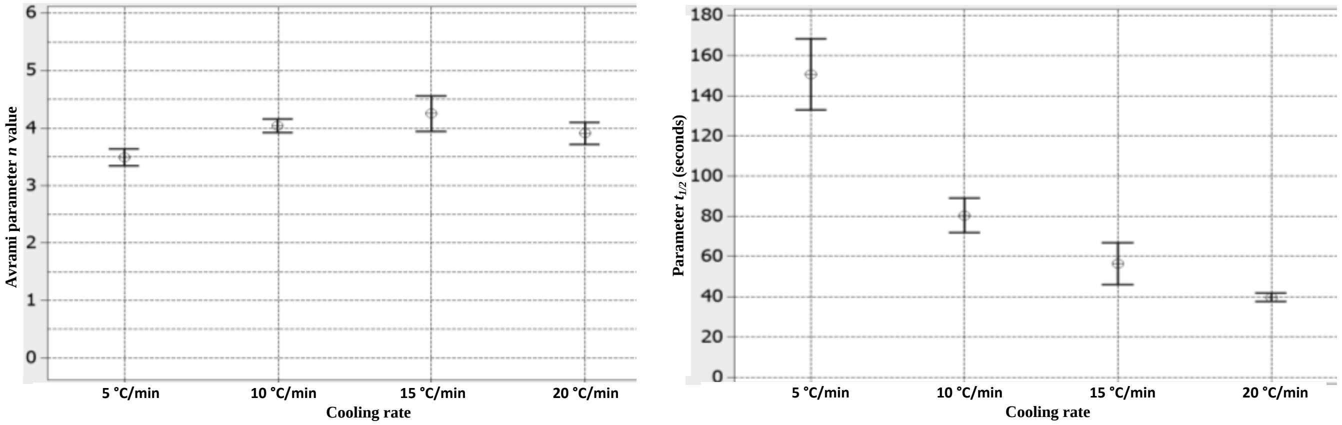


Fig. 7 Intervals (95% of confidence for the mean value) chart for the Avrami parameters: *n* (left chart) and $t_{1/2}$ (right chart) at 5, 10, 15 and 20 °C/min for bulk non-isothermal crystallization tests

The Fig. 8 shows the overlap charts of film (dashed lines) over bulk (continuous line) non-isothermal crystallization kinetics for correlation purposes.

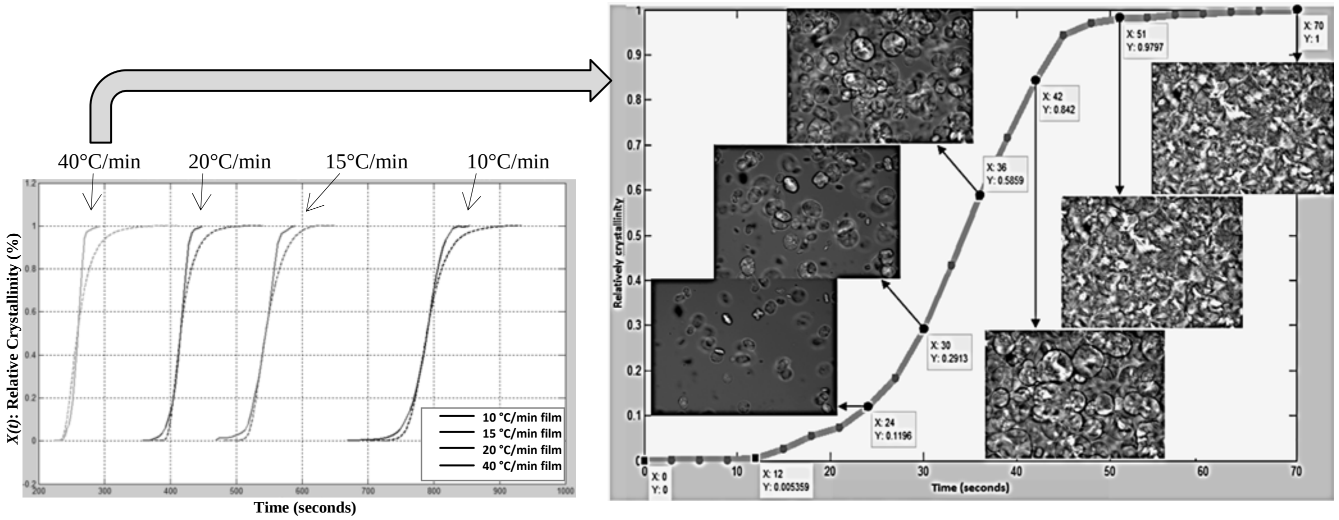


Fig. 8 Overlap of film over bulk non-isothermal crystallization kinetics at *X(t)* = 0.5 for correlation purposes (left), non-isothermal film crystallization evolution at a T_c= 40°C/min (right)

The Table 2 contains the parameter *n* determined for film tests. The values around 4 confirm and indicate a thermal nucleation with three dimensions crystal growth for non-isothermal crystallization process. In addition to that, the sequence of photos shows a thermal nucleation for all cooling speeds. Specifically for 5 °C/min the

Table 2 Avrami parameters and $t_{1/2}$ for film non-isothermal crystallization process

Cooling rate (°C/min)	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)
10	3.691	1.60818 e-08	121.1
15	4.094	3.42260 e-08	61.79
20	4.131	4.24924 e-08	56.96

thermal nucleation is hardly perceptible; this confirms the value for *n* lower than the others as reported in Fig. 7.

4.2. ISOTHERMAL CRYSTALLIZATION

The Fig. 9 shows the bulk isothermal crystallization kinetics obtained from the second of three times each specimen was run.

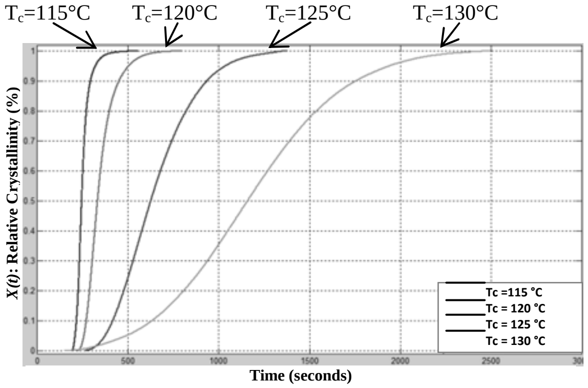


Fig. 9 Bulk isothermal crystallization kinetics at 115, 120, 125 and 130 °C

The value of the parameter *n* around 2 (see Table 3) indicates an athermal nucleation with two dimensions crystal growth for isothermal crystallization process.

Table 3 Avrami parameters and $t_{1/2}$ for bulk isothermal crystallization process at 115, 120, 125 and 130 °C

Crystallization Temperature	Test repetition	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)	Crystallization Temperature	Test repetition	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)
115 °C	1 rst time	2.637	1.82507 e-05	54.41	125 °C	1 rst time	2.131	3.16239 e-06	322.2
	2 nd time	2.601	2.20465 e-05	53.51		2 nd time	2.170	1.92696 e-06	363.7
	3 rd time	2.689	1.40563 e-05	55.51		3 rd time	2.262	8.91477 e-07	402.7
120 °C	1 rst time	2.242	2.42603 e-05	97.52	130°C	1 rst time	2.540	2.96554 e-08	794.9
	2 nd time	2.248	1.80866 e-05	109.8		2 nd time	2.479	2.42014 e-08	1008.0
	3 rd time	2.269	1.25971 e-05	123.3		3 rd time	2.346	3.70543 e-08	1248.0

The Fig. 10 contains the intervals chart at a confidence of 95 % for parameters *n* and $t_{1/2}$.

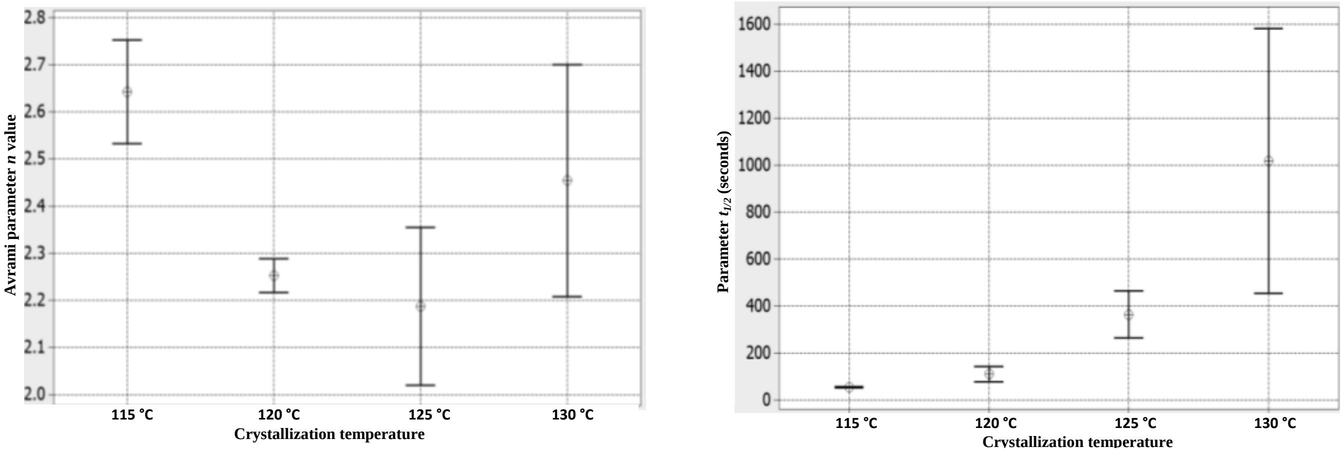
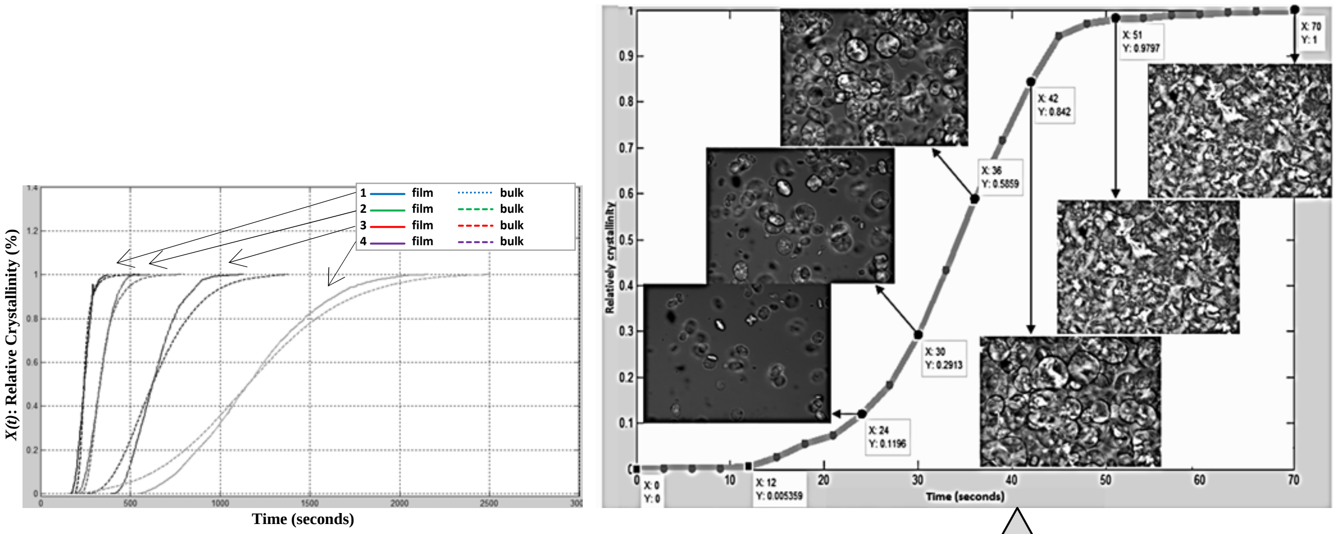


Fig. 10 Intervals (95% of confidence for the mean value) chart for the Avrami parameter: *n* (left chart) and $t_{1/2}$ (right chart) at 115, 120, 125 and 130 °C (bulk isothermal crystallization)

According to the intervals chart, the mean value of *n* seems to have no significant difference for crystallization temperature of 120, 125 and 130°C, however for crystallization temperature of 115 °C the mean value of *n* has a small increment compared to the others; this might be because at a low crystallization temperature the athermal nucleation gets maximized. The mean value of $t_{1/2}$ increases significantly as the crystallization temperature increases.

The Fig. 11 shows the overlap charts of film (dashed lines) and bulk (continuous line) isothermal crystallization kinetics for correlation purposes.



	Film test temperature set point (°C)	Bulk test crystallization temperature (°C)
1	145	115
2	150	120
3	155	125
4	160	130

Fig. 11 Overlap of film over bulk isothermal crystallization kinetics at *X(t)* = 0.5 for correlation purposes (left), isothermal film crystallization evolution at a crystallization temperature of 130°C (right)

The Table 4 contains the parameter *n* determined for film tests. The values around 2 confirm and indicate an athermal nucleation with two dimensions crystal growth for isothermal crystallization process. In addition to that, the sequence of photos shows an athermal nucleation for the crystallization temperatures of 120, 125, and 130 °C.

Table 4 Avrami parameters and $t_{1/2}$ for the film isothermal crystallization process

Set Point (Crystallization temperature)	Avrami *n*	Avrami *k* (sec^{-n})	$t_{1/2}$ (sec)
145 (115) °C	**2.392**	1.94892 e-05	80.87
150 (120) °C	**2.348**	6.19148 e-06	141.6
155 (125) °C	**2.042**	1.03115 e-05	231.9
160 (165) °C	**1.991**	1.99354 e-06	617.7

For the crystallization temperature of 115 °C, the sequence of photos revel a thermal nucleation that stops rapidly and continues with an athermal nucleation. This might be the reason for the higher mean *n* values registered in Fig. 10 for the bulk isothermal crystallization at a crystallization temperature of 115 °C. The mean value of $t_{1/2}$ increases significantly as the crystallization temperature increases.

The range variation observed in *n* and $t_{1/2}$ is mainly because of the consumption of the sample-PP each time the same specimen is run through the temperature profile several times in presence of atmospheric O_2 and the degradation of the polymer itself.

5. CONCLUSIONS

The method proposed to analyze the bulk crystallization behavior of i-PP was able to establish the type of nucleation in a reliable way as it was confirmed by the MOLP technique.

The method proposed to analyze the film crystallization behavior of i-PP by the MOLP technique from a film sample with crystallization at several levels as well as the correlation with bulk tests made possible the confirmation of the nucleation type and the form of the crystal growth. This also allows the measurement of the spherulite growth rate that can be related to the bulk crystallization.

By this way, the main objective of approaching hand-on experience to students for the polymer phase change teaching by the use of a simpler, rougher, lower cost, easier to use instrument than DSC equipment is accomplished.

Even though the comments above, the variation in the Avrami parameter n obtained in the bulk tests (Fig. 7 and Fig. 10) can be reduced by not using the same specimen to repeat the bulk test. For this, a scale to weigh milligrams is required to make different specimens with same pan and polymer content mass. This also helps in the variability reduction of the parameter $t_{1/2}$.

The method to determine the base-line is graphic and was carried out manually. The development of a computational program to do it will reduce variability but also will greatly reduce this time consuming process.

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