

## Comparative study of the effect of TiO<sub>2</sub> and ZnO on the crystallization of PHB

### Estudo comparativo do efeito do TiO<sub>2</sub> e ZnO na cristalização do PHB

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#### RESUMO

Foram preparados compósitos PHB/TiO<sub>2</sub> e PHB/ZnO num misturador interno de laboratório, a cristalização foi investigada por calorimetria exploratória diferencial (DSC), com taxas de aquecimento e resfriamento entre 5 e 30 °C/min e a superfície de fratura de seletas composições analisada por microscopia eletrônica de varredura (MEV). Através das imagens de MEV foi observado que as nanopartículas de ZnO e TiO<sub>2</sub> estão bem dispersas na matriz de PHB. Por DSC, observou-se que a adição de TiO<sub>2</sub> e ZnO modificou a temperatura e taxa de cristalização do PHB, sem afetar significativamente a cristalinidade total. Em geral, a adição da carga TiO<sub>2</sub> promoveu alterações mais significativas na matriz de PHB, comportando-se como um agente nucleante.

**Palavras-chave:** PHB, cristalização, TiO<sub>2</sub>, ZnO, DSC.

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#### ABSTRACT

PHB/TiO<sub>2</sub> and PHB/ZnO compounds were prepared in a laboratory internal mixer. Crystallization was investigated by differential scanning calorimetry (DSC) with heating and cooling rates ranging from 5 to 30 °C/min. Fractured surface of selected samples was analysed by scanning electron microscopy (SEM). From the SEM images, it was observed that ZnO and TiO<sub>2</sub> nanoparticles were properly dispersed in the PHB matrix. DSC studies revealed that the addition of TiO<sub>2</sub> and ZnO changed the temperature and crystallization rate but did not affect the total crystallinity significantly. In general, TiO<sub>2</sub> behaved as nucleating agent greatly influencing the PHB crystallization.

**Keywords:** PHB, crystallization, TiO<sub>2</sub>, ZnO, DSC.

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#### 1. INTRODUCTION

Petroleum is the main resource to produce polymers and it is non-renewable, in its production, many pollutants gases are emitted, responsible for a large production of leavings, which leads to environmental disasters. Therefore, it is necessary to provide alternative resources to supply the polymer industry. Biodegradable polymers have been considered as a promising alternative to avoid environment damages. These polymers have proper properties for diverse applications, e.g. automotive industry, biomedical and packaging sectors.

Polyhydroxyalkanoates (PHA)s are biodegradable thermoplastics and have similar properties as those presented by polymers derived from petroleum, an example is the poly(3-hydroxybutyrate) (PHB) which has similar mechanical properties to polypropylene (PP) but it is obtained from renewable resources, produced by bacterial fermentation of sugars [1-3]. PHB is biocompatible and biodegradable and has a wide range of applications in biomedical and industrial procedures. Furthermore, its processing can occur by various conventional techniques such as extrusion, injection and others [4-5].

Due to its high crystallinity, the final properties of PHB are related to the processing conditions and

crystallization mechanisms developed during it. PHB is thermally unstable, possibly degrading when submitted to usual process conditions, for instance temperatures near to its melting point ( $\approx 180^{\circ}\text{C}$ ). Thus, studies of processing conditions and the crystallization process are necessary for understanding and controlling the properties of the final product. Researches are being conducted with the objective to optimize those conditions [6-10]; there are previous works with neat PHB, PHB/PS blends, PHB/carbon black and PHB/babassu composites, the improvement of PHB properties, the increase in thermal stability upon addition of carbon black, decrease in crystallinity degree with PS addition, rational crystallization control through applying defined heating/cooling DSC rates were reached in our works [6-10].

PHB frequently shows relatively large spherulites, due to its low nucleation rate [11]. The disadvantages related to its oversized spherulites, such as brittleness and mechanical performance loss, can be avoided by the introduction of fillers and inorganic additives, which improve toughness and electrical and magnetic properties [12]. Investigations were realized about the usage of PHB in many compounds, such as PHB/talc, PHB/polyethylene terephthalate (PET), PHB/polyamide 11 (PA 11), PHB/carbon black, and it was observed a faster crystallization from the molten [13]. Therefore, in this work titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide (ZnO) were added to PHB as a methodology to obtain compositions with better properties.

$\text{TiO}_2$  and ZnO are inorganic pigments with microbial properties and UV protection [14], non-toxic and thermally stable, easily dispersible within polymeric matrix [15-17]. It is expected that  $\text{TiO}_2$  and ZnO modify the PHB crystallization and contribute to its microstructural control.

The aim of this work is to accomplish a comparative study of the effect of  $\text{TiO}_2$  and ZnO on the crystallization of PHB. Composites of PHB/ $\text{TiO}_2$  and PHB/ZnO with concentrations of  $\text{TiO}_2$  and ZnO ranging from 0 to 10% in weight were produced by melt mixing; the crystallization was analysed by differential scanning calorimetry (DSC) with heating rates among 5 and  $30^{\circ}\text{C}/\text{min}$ .

## 2. MATERIALS AND METHODOLOGY

### 2.1 Materials

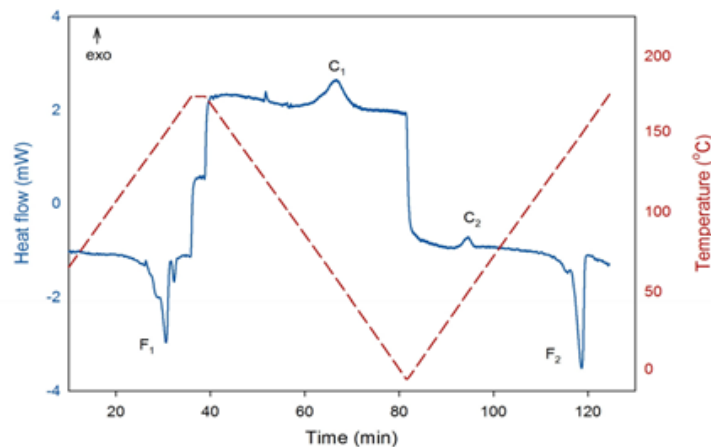
PHB samples were provided by PHB Industrial SA (Brasil).  $\text{TiO}_2$  was bought from Evonik Degussa Co. with surface area of  $50\text{ m}^2/\text{g}$  and 75:25 proportion of anatase to rutile, crystal size range from 25 to 94 nm. ZnO was acquired from Acros Organics (99.5% purity), specific surface area of  $28\text{ m}^2/\text{g}$ . Before mixing, PHB,  $\text{TiO}_2$  and ZnO were oven dried at  $80^{\circ}\text{C}$  for 6h.

### 2.2 Methodology

The compounds were produced by mixing in a rheometer Haake Rheomix 600 unit for 10 min, with a wall temperature of  $180^{\circ}\text{C}$ , and velocity of 60 rpm using high intensity rotors. Compositions of  $\text{TiO}_2$  and ZnO ranged from 0 to 10% in weight.

Scanning electron microscopy (SEM) images were obtained in a LEO 1430 of Zeiss. Samples were fractured in liquid nitrogen and after that, images were obtained at the fractured surface. All the samples were coated with a layer of carbon.

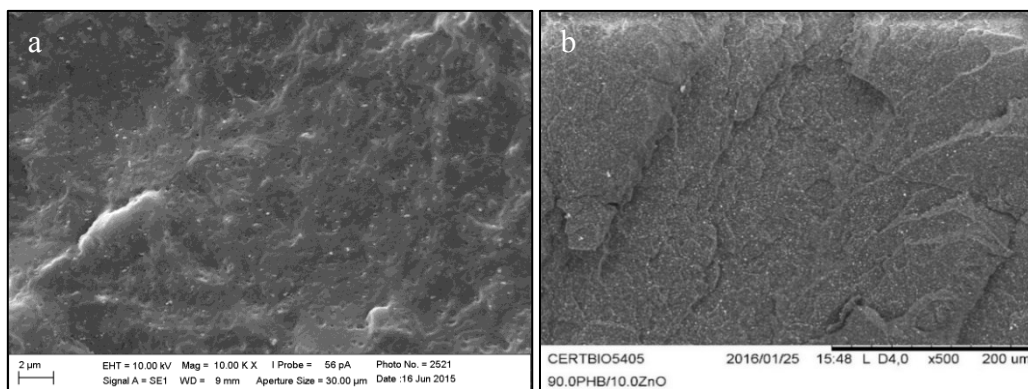
DSC analyses were acquired in a TA Instruments DSC Q20, under a nitrogen flow of  $50\text{ ml}/\text{min}$ . Utilized samples of 5 mg coated with aluminium foil. The thermal cycles were composed of four stages: (1) the samples were heated from room temperature ( $\sim 23^{\circ}\text{C}$ ) to  $190^{\circ}\text{C}$  (first heating); (2) keeping at this temperature for 3 min (isothermal process); (3) the molten mass was cooled to  $20^{\circ}\text{C}$  (first cooling) and then, (4) the sample was reheated to  $190^{\circ}\text{C}$  (second heating). Figure 1 shows a typical DSC curve with the cycles indicated. Four thermal events have been identified in most DSC tests, melting during the first heating ( $F_1$ ), crystallization by the molten while cooling ( $C_1$ ), cold crystallization during the reheating ( $C_2$ ), and second melting ( $F_2$ ). The experiments were conducted at constant rates of heating/cooling 5, 7.5, 10, 15, 20 and  $30^{\circ}\text{C}$ .



**Figure 1:** Typical DSC curve of PHB heating/cooling/reheating at 6 °C/min, showing the phase changes: first melting (F<sub>1</sub>), crystallization from the molten state (C<sub>1</sub>), cold crystallization (C<sub>2</sub>), and second melting (F<sub>2</sub>).

### 3. RESULTS AND DISCUSSION

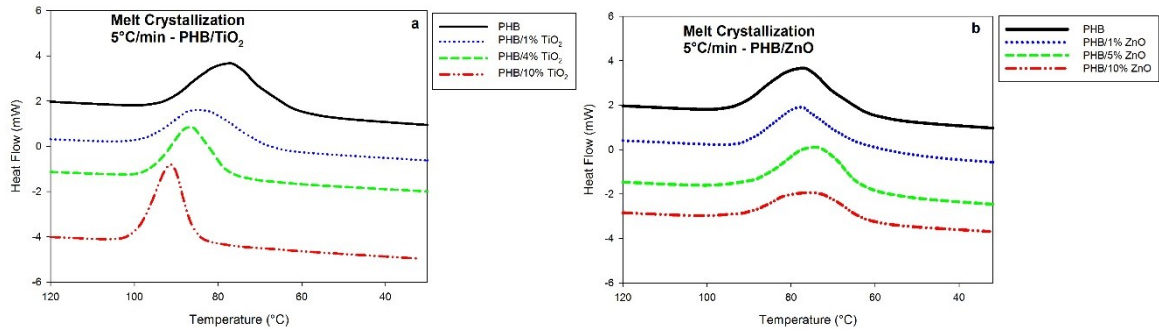
Figure 2 shows SEM images for PHB/TiO<sub>2</sub> and PHB/ZnO composites. The homogeneous dispersion of the particles in the PHB matrix, without agglomerates, is indicative for an efficient processing. Apparently, particles are bonded to PHB matrix, implying a good adhesion between the fillers and the polymeric matrix.



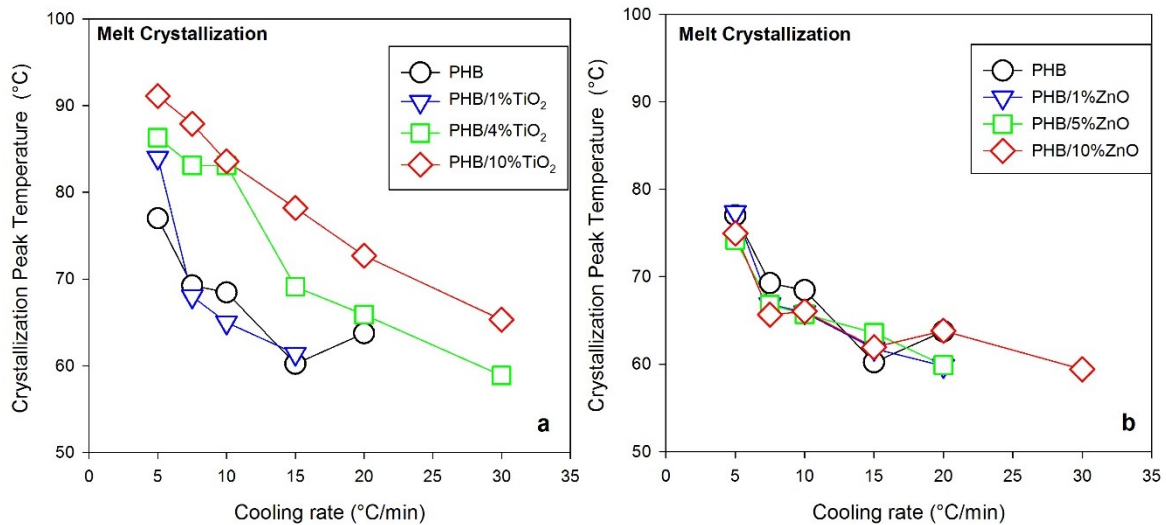
**Figure 2:** SEM images of compounds PHB/10% TiO<sub>2</sub> (a) and PHB/10% ZnO (b).

Figure 3 shows DSC curves of PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites for crystallization from the melt at a cooling rate of 5 °C/min. A displacement of the crystallization exotherms to higher temperatures is observed for the composites with TiO<sub>2</sub>, indicative of nucleating activity of TiO<sub>2</sub> in PHB. The nucleating effect of ZnO is less evident for PHB/ZnO compounds as the crystallization exotherms show similar peak temperatures as neat PHB.

Figure 4 shows the dependence of the peak melt crystallization temperature for PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites. It is noted that the filler content of TiO<sub>2</sub> influenced the crystallization temperature (except for composite with 1% of filler); and the effect is bigger at higher cooling rates. The content of ZnO does not affect significantly the crystallization temperature of PHB.



**Figure 3:** DSC curves for PHB and its compounds during crystallization from molten under a cooling rate of 5 °C/min. (a) PHB/TiO<sub>2</sub> (b) PHB/ZnO.



**Figure 4:** Peak crystallization temperature from molten for PHB, PHB/TiO<sub>2</sub> (a) and PHB/ZnO composites (b).

Figure 5 displays the maximum melt crystallization rate ( $C_{max}$ ) of PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites. PHB/ZnO system did not exhibit significant changes, however, composites with TiO<sub>2</sub> greater increases at  $C_{max}$  were achieved for higher contents of TiO<sub>2</sub> and higher cooling rates.

Figure 6 exhibits the crystallinity during cooling for PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites. There was a crystallinity decrease at higher cooling rates for TiO<sub>2</sub> and ZnO composites. Considering a constant cooling rate, adding ZnO to PHB did not modify significantly the crystallinity, except for composites with 10% of fillers; for TiO<sub>2</sub> composites, crystallinity changes were observed for filler levels higher than 1%.

Researches have been performed about the effect of TiO<sub>2</sub> and ZnO on the crystallization of polymer resins. WU et al. [18], LIU et al. [19] and HE et al [20] investigated the nonisothermal melt crystallization of PA11/ZnO nanorod, Poly( $\epsilon$ -caprolactone) (PCL)/ZnO and PET/ZnO, respectively, it was verified a displacement of the crystallization exotherms to lower temperatures increasing the cooling rates. Regarding the effect of ZnO, in composites with PA11 it was observed an increase of  $\tau_{1/2}$  (time to reach 50% of crystallized mass), whereas in PCL/ZnO and PET/ZnO the melt crystallization rate increased upon addition of ZnO, which behaves as a nucleating agent.

SUPAPHOL et al. [21] and WANG and ZHANG [22], studied the influence of TiO<sub>2</sub> on the melt crystallization of isotactic Polypropylene (iPP) and High Density Polyethylene (HDPE), respectively, lower values of  $\tau_{1/2}$  were found in iPP/TiO<sub>2</sub> and HDPE/TiO<sub>2</sub> composites. CAYUELA et al. [23] analyzed the effect of TiO<sub>2</sub> on the cold crystallization of PET and higher crystallization rates were reached in PET/TiO<sub>2</sub> composites. Summing up, data gathered in the literature agree with these presented in this paper.

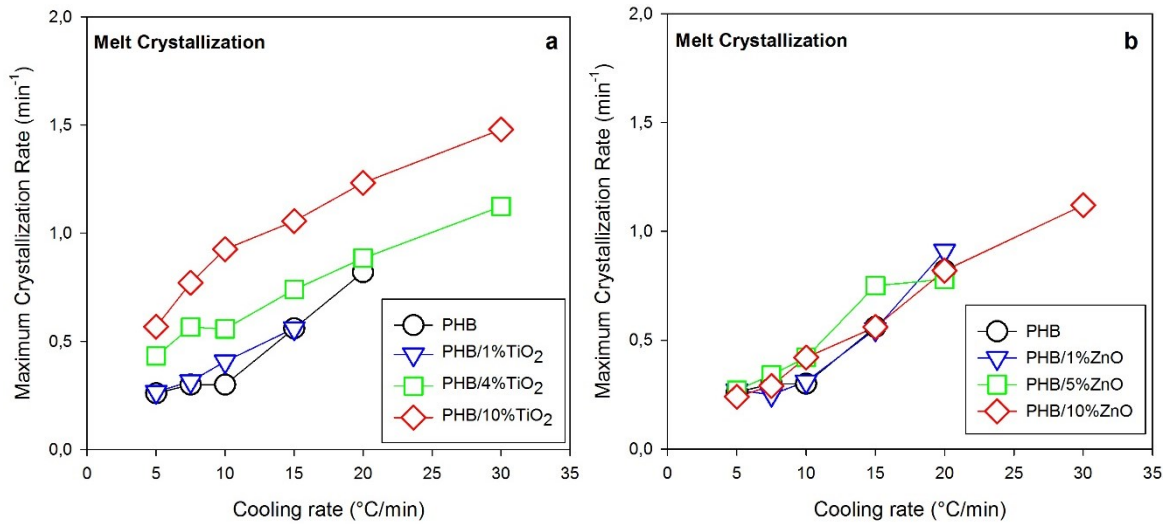


Figure 5: Maximum melt crystallization rate of PHB, PHB/TiO<sub>2</sub> (a) and PHB/ZnO (b).

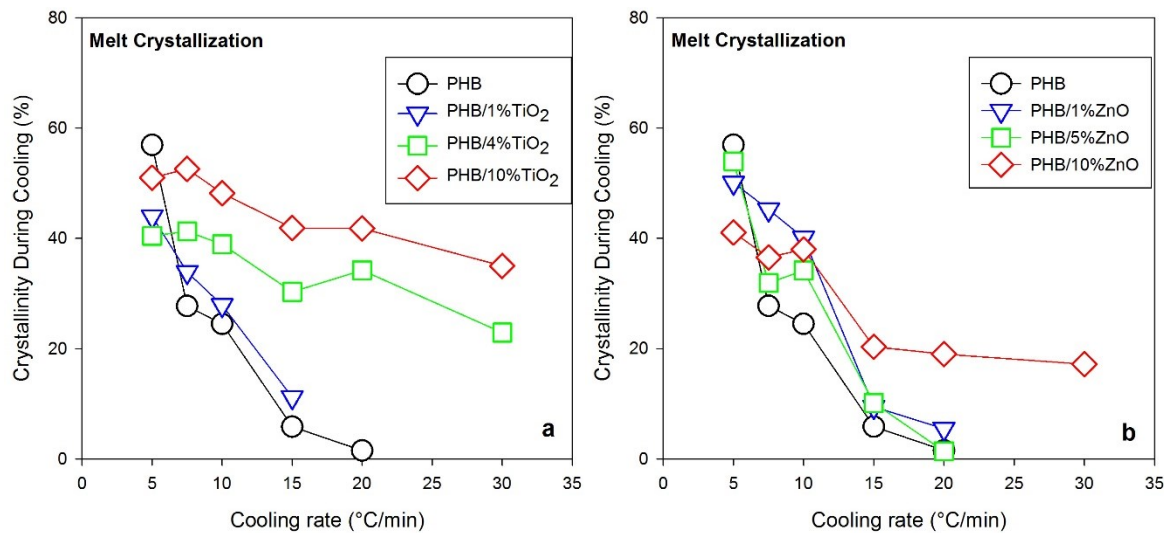
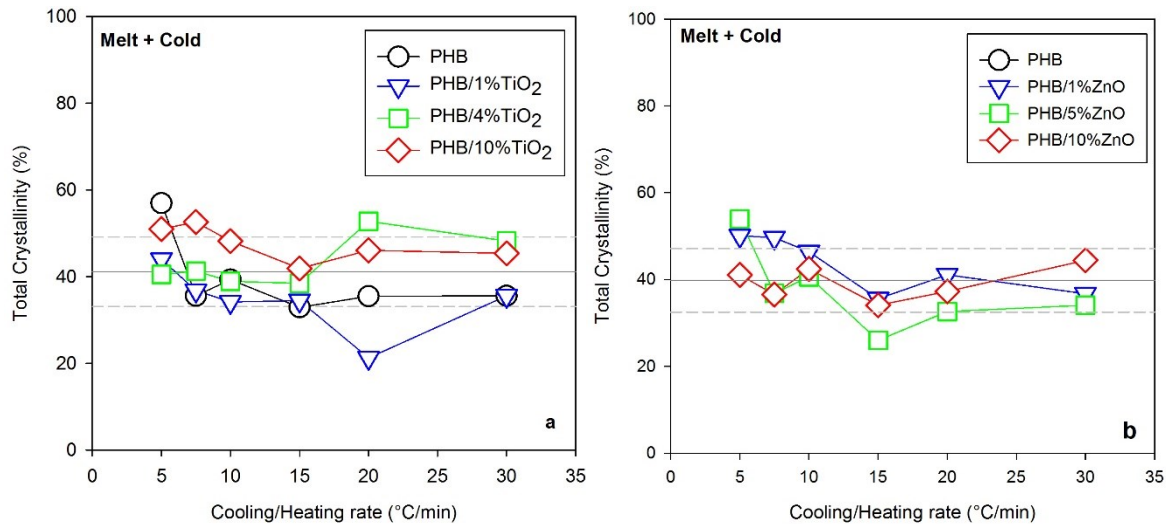


Figure 6: Crystallinity after cooling for PHB, PHB/TiO<sub>2</sub> (a) and PHB/ZnO (b).

During cold crystallization, TiO<sub>2</sub> and ZnO did not change significantly the peak temperatures and maximum crystallization rate. However, for crystallinity, a small variation due to fillers levels could be observed. That behaviour might be related to the differences between melt crystallization -liquid state and from the cold crystallization -glassy state.

The total crystallinity (sum of developed crystallinity during cooling and heating cycles) for PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites is exhibited at Figure 7. Total crystallinity, 40 ± 8%, does not depend on heating/cooling rate nor filler type/content, which suggests that the utilized fillers change crystallization process without influencing the amount of crystallized mass.





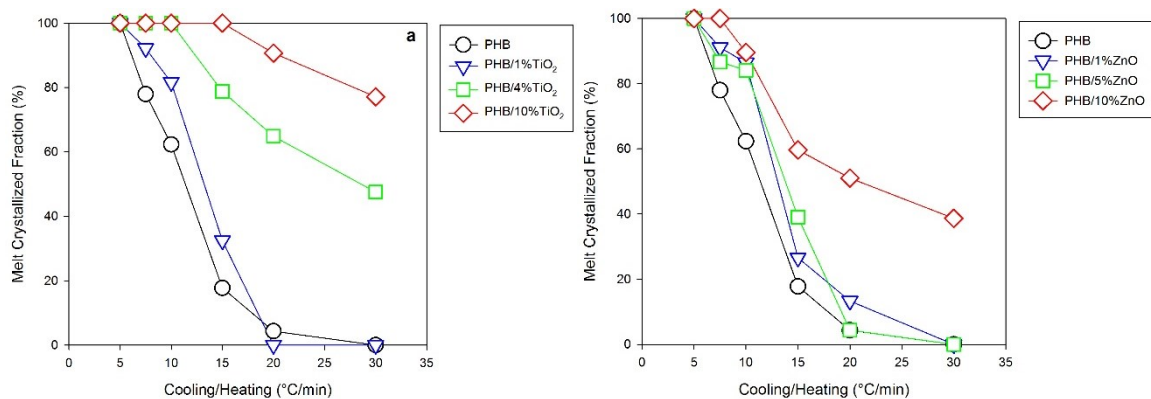
**Figure 7:** Total crystallinity (melt + cold crystallization) for PHB, PHB/TiO<sub>2</sub> (a) and PHB/ZnO (b) composites.

The equilibrium between melt and cold crystallization is analysed in terms of crystallized fraction for PHB in each event at a specific test, according to Eq. (1):

$$f_M = \frac{\Delta X_c(C_1)}{\Delta X_c(C_1) + \Delta X_c(C_2)} \quad f_c = \frac{\Delta X_c(C_2)}{\Delta X_c(C_1) + \Delta X_c(C_2)} = 1 - f_M \quad (1)$$

Where:  $f_M$  e  $f_c$  are fractions of crystallized mass from the molten and glassy states, respectively and  $X_c(C_1)$  e  $X_c(C_2)$  are observed crystallinities after melt and cold crystallizations.

Figure 8 presents curves of crystallized fractions from the molten in function of cooling rates for PHB, PHB/TiO<sub>2</sub> and PHB/ZnO composites. The crystallized fraction depends on the cooling rate during crystallization; as the rate increases the crystallized fraction decreases during cooling process and the crystallized fraction increases during reheating (cold crystallization). Adding TiO<sub>2</sub> levels higher than 1%, leads to a substantial effect of the crystallized fraction on the cooling/heating rate, promoting the melt crystallization. A similar behaviour occurs with ZnO composites, although a positive effect on the crystallization is only observed for composites with ZnO levels higher than 5%.



**Figure 8:** Crystallized fraction from the molten versus cooling rate for PHB, PHB/TiO<sub>2</sub> (a) and PHB/ZnO (b).

#### 4. CONCLUSION

The processing used resulted in a good dispersion of TiO<sub>2</sub> and ZnO nanoparticles within PHB matrix. The addition of ZnO nanoparticles had a lower influence on PHB crystallization, the filler had no notable effect on the total crystallinity nor at PHB crystallization rate. The addition of TiO<sub>2</sub> accelerated greatly PHB crystallization, the crystallization rate increased with the filler content, which behaved as nucleating agent. Results suggest that microstructure control and PHB properties can be achieved by changing the heating/cooling rates and/or adding inorganic fillers.

## 5. ACKNOWLEDGEMENT

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