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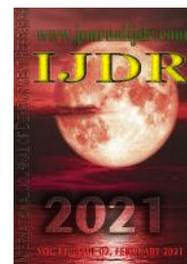
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RESEARCH ARTICLE

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EFFECT OF SILICON DIOXIDE IN THE PHB MATRIX CHARACTERISTICS

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ABSTRACT

Poly (3-hydroxybutyrate) is a biopolymer produced mainly by microorganisms of *Alcaligenes*, *Azobacter*, *Bacillus* and *Pseudomonas* genera. Due to its properties such as high degree of crystallinity, crystalline melting temperature and barrier properties this polymer has the potential to replace polyolefins, with the advantage of being biodegradable, biocompatible, and from a renewable source. In this work were prepared a nanocomposites with two kinds of silicon dioxide (hydrophilic or hydrophobic) employing solution casting method. The nanocomposites obtained were characterized by XRD, DSC, and Low Field NMR (T1H). The incorporation of the two silicon dioxide types in the PHB matrix induced different and specific changes in the PHB matrix. It could be observed that silica A200 acted as nucleating agent for PHB, affecting its crystallization kinetics. On the other hand, silica R972 interacted chemically with the matrix, affecting more significantly the matrix crystalline planes. From thermal properties studied, only it was observed significant changes on the crystallization temperature for PHB/A200 systems. Evaluating the NMR relaxation data, they revealed that the PHB/R972 systems presented an interfacial chemical interaction with the matrix. On other hand, PHB/A200 systems presented a decrease of T1H relaxation time values that point to a decrease of crystal size, which shows in an increase in the molecular mobility. So, the systems analyses showed distinct characteristics and properties according to the nature of the nanoparticle incorporated in the polymer matrix, reflecting on the interaction nanoparticle/matrix degree and so on its morphologies and properties.

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INTRODUCTION

Poly (3-hydroxybutyrate) (PHB) is a polymer synthesized mainly by microorganisms of *Alcaligenes*, *Azobacter*, *Bacillus* and *Pseudomonas* genera. It has a predominantly isotactic structure, forming an orthorhombic cell in solid state, crystallinity above 55 % and a molar mass from 50,000 to 1,000,000 Daltons. The main difference among PHB and other polyhydroxyalkanoates is the presence of the chiral center in position 3, which is mainly responsible for its physical properties and the action of the enzymes involved in its biosynthesis and biodegradation. Due to its properties, this polymer has the potential to replace polyolefins, with the advantage of being biodegradable, biocompatible and from a renewable source. Its glass transition temperature (T_g) is around 5 °C while its crystalline melting temperature (T_m) is around 180 °C, having thus, similar properties to those found in polypropylene. It also has higher barrier properties compared to poly(ethylene terephthalate) - PET, and poly(vinyl chloride) - PVC. Its main drawback is the narrow range of thermal processing.

These characteristics make PHB an interesting alternative for applications both in the medical-pharmaceutical area, for the manufacture of suture threads, bone prostheses and controlled release of drugs as well as in the packaging area. However, it is a fragile material, brittle and more expensive than commodities. Therefore, the use of new technologies, such as nanotechnology, makes it possible to introduce modifications in this polymer to change its processing characteristics and consequently its applications (Avella et al. 2001; Pandey et al. 2005; De Paula, Campos, and Mano 2014; Reis et al. 2008; Rosa et al. 2003; Sudesh, Abe, and Doi 2000). Nanoscience and nanotechnology have presented such as an important alternative to traditional sciences because the properties manifested in the nanoparticles differ significantly of those found in microparticles and macroparticles. The high surface area of the nanoparticles provide modification of intra and intermolecular interactions, so that allows modifying or incorporate new properties or even increase intensity of the response to a given energy applied to the material containing low nanoparticle concentration when compared to traditional composites, justifies the growing interest in this field (Almeida 2010; Carn et al. 2010; Ding et al. 2014). Modifying chemical environment can lead to the emergence of new or modified properties in nanoparticles. Silicon

dioxide has been used due to its proven influence on mechanical strength in several polymers because of its action inside the crystalline region of these materials. A major challenge in nanotechnology is the dispersion of nanoparticles. The high relative surface area and the high interaction between them cause agglomeration, making the nanofillers behave like a micro or macroparticles, reducing its potential to alter matrix properties. Depending on the chemical modification applied to silicon dioxide, it can become hydrophobic, changing the way it interacts with the medium in which it is present (Esteves, Barros-Timmons, and Trindade 2004; Gómez-romero 2001; Passos et al. 2011; Sanchez et al. 2005; Silvério 2009). Thus, the main objective of this work was to understand the influence of the incorporation of two silicon dioxide types (hydrophilic and hydrophobic) by solution casting method on the crystallinity and molecular mobility of PHB matrix. For that the systems were mainly characterized by X-ray diffraction (XRD), Nuclear Magnetic Resonance in the time domain (TDNMR) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Solvent choice: The solubility of poly (3-hydroxybutyrate) purchased from the PHB industry was tested with tetrachloroethane (TCE), dichloromethane (DCM), tetrahydrofuran (THF) and chloroform, with a degree of purity PA aiming at the formation of polymeric film with less toxicity and less time for the total evaporation of the solvent. The solvent chosen was chloroform. Although the solubilization in TCE occurred in less time at lower temperatures, it requires heating or a long time for its total elimination in the polymeric film, which can vary from one to three weeks, depending on the thickness of the film. Chloroform has less toxicity and is easier to control its evaporation to obtain films, in addition to being a solvent already used industrially, including in the extraction of PHB itself. The choice corroborates with the research done in the literature that it is the most used solvent (BLAZEK 2012; Paula, Campos, and Mano 2014; Savenkova et al. 2000).

Preparation of nanocomposites: The PHB was solubilized in chloroform for 24 h at room temperature, with subsequent heating at 40 ° C for additional 2 h under constant magnetic stirring. The total mass / volume ratio of solvent was 5%. To prepare the nanocomposite systems, two silicon dioxide nanoparticle types were used. Aerosil®200 with a specific area of 200 ± 25 m²/g and an average size of 12 nm and Aerosil®R972 a hydrophobic dimethyl-dichlorosilane modified silicon dioxide with a specific area of 110 ± 20 m²/g and average particle size of 16 nm. The nanoparticles were dispersed in chloroform, in compositions containing 0.2, 0.5, 0.75 and 1% of the mass of silicon dioxide relative to the total mass of solids, by means of 135 W ultrasound at room temperature for 30 min in a closed system. The polymeric solution was added to the silica/solvent dispersion in order to minimize losses. The masses solubilized in this way totaled 4g for the polymer/silica pair. The systems followed the mixing and heating process previously described. After mixing the solutions, they were poured into Petri dishes, with partial sealing and left on levelled plates under fume hood vapors extraction at room temperature. The slow exit of the solvent was accompanied by the loss of mass of the films obtained until constant mass (Monteiro et al. 2012).

Characterization: The films obtained were characterized by X-ray diffraction using an Ultima IV X-ray diffractometer from Rigaku Corporation with CuK α radiation (0.154 nm, 40 Kv, 120 mA) at room temperature, scanning over a 2 θ range from 2 to 40° with a 0.05 step, at a rate of 1°/min. Crystallinity measurements were obtained by XRD deconvolution. All calculations were performed using Fityk software and the peaks were deconvoluted using Gaussian peak function; differential scanning calorimetry in a TA Instruments DSC Q1000 in the temperature range of -40°C to 200°C, at heating rate of 5 °C/min, followed by rapid cooling, a second heating cycle at 5 °C/min and subsequent cooling at 5 °C/min. The equipment was calibrated with Indium (In). The crystalline melting temperature (T_m) and glass transition temperature (T_g) were determined in the first heating and

the crystallization temperature (T_c) during the cooling of the system. Time domain nuclear magnetic resonance was carried out in a MARAN Ultra 23 Resonance-Oxford Spectrometer. Time domain NMR was used to determine the relaxation times of the hydrogen nuclei, T₁H, using the inversion-recovery pulse sequence. The pulse used was 90° automatically calibrated to 4.7 microseconds. Four accumulations were made for each sample. The FID obtained for 40 values ranged from 0.01 to 5000 ms.

RESULTS AND DISCUSSION

X-Ray Diffraction: PHB is highly crystalline; however when nanoparticles are incorporated in PHB matrices, they can induce modifications in its crystalline planes, favoring certain structures, which is reflected in its degree of crystallinity, in the transition temperatures and, consequently, in the molecular mobility of chains. To assess the behavior of hybrid PHB/SiO₂ systems, an analysis of the XRD of the matrix, the nanofillers and the prepared systems was performed, as observed in Figures 1 and 2.

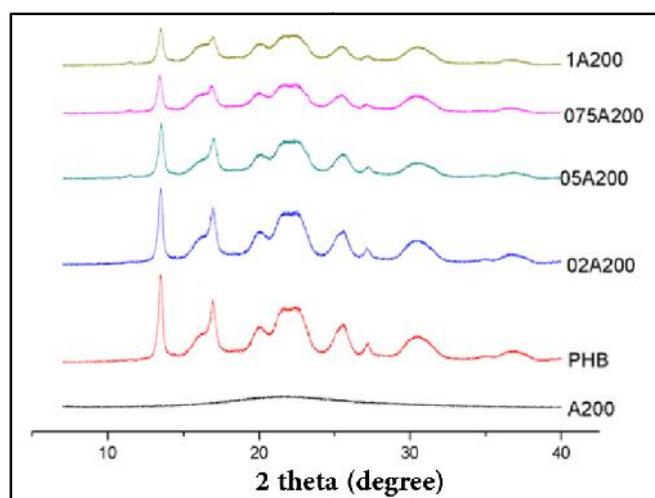


Figure 1: Diffractograms of PHB, A200 silica and hybrids with A200

The XDR profile in Figure 1 show the PHB crystalline planes, highlighting the Miller index (020) = 13.5°; (110) = 17°; (021) = 20°; (101) = 22°; (130) = 25.5°; (040) = 27°; (002) = 30.7° (Mottin et al. 2016); the amorphous halo of silica A200 and a progressive reduction in the intensity of the PHB crystalline planes and simultaneous widening along with the increase of the silica A200 content for all hybrids compared to pristine matrix. This behavior points to an interference in the crystallization process, generating a material with less crystalline organization.

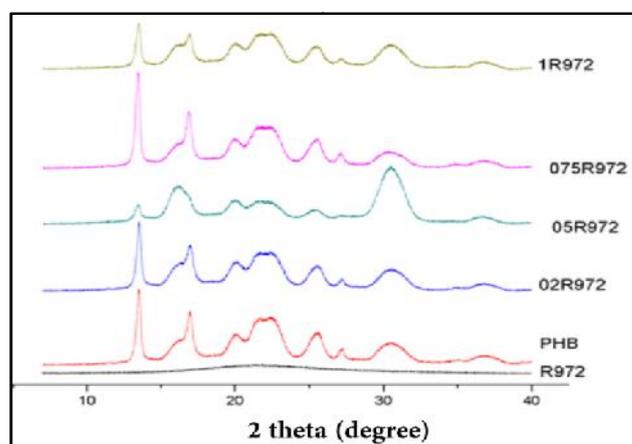


Figure 2. Diffractograms of PHB, R972 silica and hybrids with R972

The samples with silica R972 behaved differently from those containing silica A200 according to the XDR profile (Figure 2),

showing a random behavior of favoring the crystalline planes. This is probably due to its better dispersion caused by its organic modification. For sample 02R972, there was no significant change in peak intensity and width. However, for sample 05R972 there is a distinct distribution of the intensity of the crystalline planes 30.7° (002) as well as a significant decrease in the plane located at ~ 13° (020) (Mottin et al. 2016). Also is possible to observe a change position from 17° to 16°, point out to changes in this crystalline plane, increase in the peaks located at 17° (110) and indicating that there was a more pronounced change in the morphology of the crystals pointing to a new structural organization of this material due to the torsions and interactions with the silica. The addition of 0.75 wt.% of R972 (075R972) promoted the return of the structural organization own characteristic of PHB with an intensity increase of the (020) peak and a small decrease of intensity in the (101) and (002). The increase in the silica concentration to 1 wt.% promoted the formation of heterogeneous material that can be proven by the decrease in (020) and (101) peaks intensities and the increase in the (002), these variations may be related to the amount of silica introduced that promote multiple interactions in the system. The degree of crystallinity of hybrid systems containing is listed in Table 1.

Table 1. Crystallinity Degree Index of A200 Composites

Sample	c (% ± 2%)
PHB	62
02A200	62
05A200	56
075A200	61
1A200	62
02R972	69
05R972	59
075R972	62
1R972	55

According to the data listed in Table 1, for the systems containing A200 the composition containing 0.5% silica presented the lowest degree of crystallinity, which can be attributed to the interference of silica in the PHB crystallinity process. On the other hand, the systems containing R972 present changes in all composition studied except for 075R972. The better result of the silica contribution in the interference of crystallinity process could be attributed by good interaction between particle and polymer matrix due to chemical modification with dimethyl-dichlorosilane favoring a good dispersion and distribution of these particles in the matrix. However, for the composition 99.8/0.2 there was an inverse effect, resulting in an increase in the degree of crystallinity, which indicates that in this concentration the silica favored the interchains interaction, leading to the formation of larger crystals or with less defects. To assist in the elucidation of the silica interference in the PHB matrix, the DSC technique was used to observe the thermal behavior of the nanocomposites and also a possible action of the silica in the PHB crystallization dynamics observed in the XRD.

Differential Scanning Calorimetry (DSC): The DSC technique was used to determine the crystallization temperature (T_c) (Figures 3 and 4, Table 3), the glass transition temperature (T_g) and the crystalline fusion temperature (T_m) (Table 4).

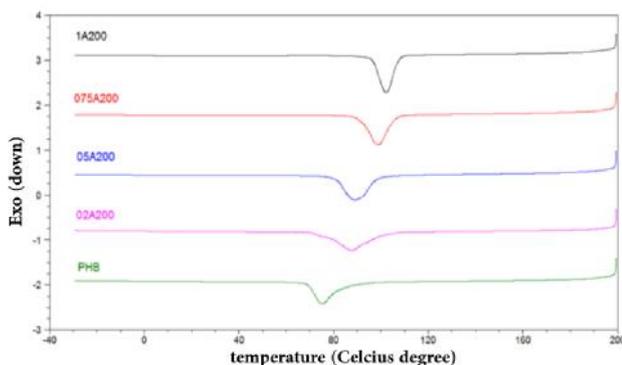


Figure 3: Crystallization Curve for PHB and its hybrids PHB/A200

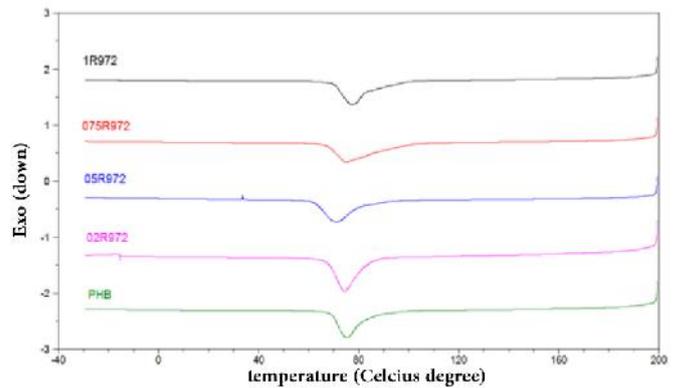


Figure 4. Crystallization curves for PHB and its PHB/R972 composites

Table 3. Crystallization temperatures of A200 composites

Sample	T_c ($\pm 2^\circ\text{C}$)
PHB	75
02A200	88
05A200	89
075A200	99
1A200	102
02R972	74
05R972	71
075R972	75
1R972	77

All the samples containing A200 silica (02A200, 05A200, 075A200, 1A200) exhibit higher crystallization temperatures higher than that observed for pure PHB. Also it was seen a tendency to increase T_c temperature with progressive increase of A200 silica, indicating a greater crystallization capacity of the systems containing these particles compared to the pristine polymer. This behavior indicates that the crystallization process was anticipated in relation to the cooling process during the thermal treatment, when compared to pure PHB, due to the presence of silica, which may reflect its action as a nucleating agent. The addition of R972 silica do not induced changes at the crystallization process. This behavior can be explained on its organic modification, which makes it difficult to act as a nucleating agent due to the strong interaction between the particles and the polymeric matrix. However, there is a subtle tendency to low temperature degree in the crystallization process only for sample 05R972.

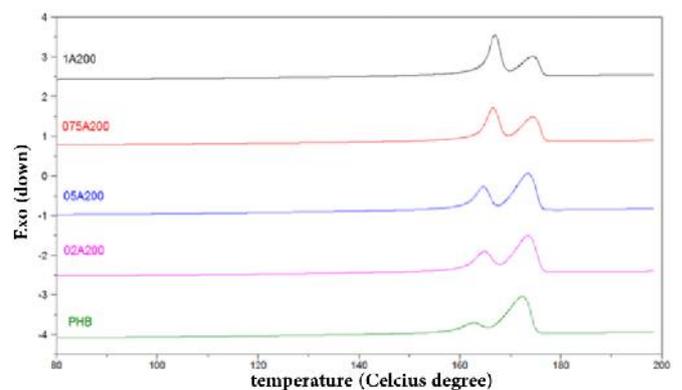


Figure 5. Crystalline melting curves of PHB and its hybrids PHB/A200

From crystalline melting scans show in Figures 5 and 6, it was observed that the heating curves of all PHB samples exhibit two crystalline melting endothermic peaks. This profile is already known and results from the existence of two crystalline populations in this polymeric matrix. Crystals that melt at lower temperatures are characterized by being smaller and / or more imperfect, and crystals

that melt at a higher temperature are larger and / or more perfect (Seoane et al. 2016). The crystalline melting curves of samples containing A200 (Figure 5) show a change in the sizes of the crystals along silica incorporation. It was observed that the increase in A200 silica incorporation favors the formation of smaller crystals, which corroborates the postulation made in the analysis of the Tc curves that the load may be acting as a nucleating agent, considering that it is reported in the literature that the increase in the concentration of nucleating agent may decrease the size of the crystal due to the increase in the number of nuclei (AMICO et al., 2011; SARZI; FELISBERTI, 2009). The crystalline melting curves of the samples containing R972 (Figure 6), did not present significant changes of crystal sizes, contrary to what was observed for the A200 system, indicating that R972 does not affect the crystal morphology and does not act as nucleating agent, suggesting that it did not act in this way in the matrix due to the organophilization process of silica which hinders this effect.

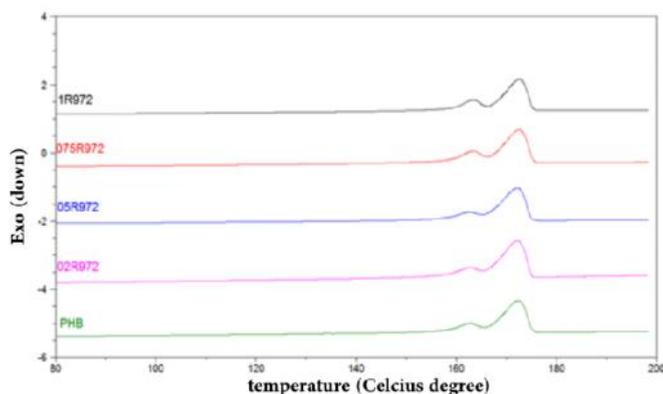


Figure 6. Crystalline melting curves for PHB and its PHB/R972 hybrids

Tables 4 show the transition temperatures of the hybrids with silica A200 and silica R972. According to DSC results (Table 4) all hybrids do not present significant changes in Tg and Tm considering the error of analysis equipment. These results suggest that the changes occur only in the crystallinity morphology such as size and perfection of crystals.

Table 4. Thermal transitions for the A200 hybrids

Sample	T _g (± 2°C)	T _{m1} (± 2°C)	T _{m2} (± 2°C)
PHB	0.8	163	172
02A200	1.6	165	174
05A200	2.2	165	174
075A200	N/A	167	175
1A200	N/A	167	175
02R972	1.0	163	172
05R972	0.2	162	172
075R972	0.8	163	173
1R972	0.9	163	173

Due to its bacterial origin, high mass, high structural regularity, and high crystallinity, PHB has high molecular rigidity. These characteristics can make it difficult to interpret the nanoparticle action in this matrix. Time domain NMR has proved to be an important tool for analyzing nanocomposites due to its high sensitivity and variety of techniques, standing out in the analysis of mobility on a molecular scale.

NMR relaxometry: The values of the spin-lattice relaxation time parameter (T₁H) were determined in order to understand the behavior of the interaction between the silica nanoparticles and PHB matrix and consequently, the dispersion and distribution of the two types of silica incorporated into PHB matrix. Table 5 show the relaxation values of the hydrogen nuclei determined for the PHB silica samples containing the A200 and R972 silica.

Table 5. Relaxation times for the PHB/A200 hybrids

Sample	T ₁ H (~ ± 2%)
PHB	632
02A200	642
05A200	623
075A200	601
1A200	605
02R972	624
05R972	644
075R972	657
1R972	720

The Table 5 shows that the addition of silica A200 in the PHB matrix generated change in the molecular dynamic behavior of the obtained systems. It was observed a subtle increase in the relaxation time for the composition 99.8 / 0.2 and a decrease for the other compositions. The increase in the T₁H value found for the 99.8 / 0.2 system indicates a slight decrease in its molecular mobility due to a good dispersion and interaction of the silica with the PHB matrix at molecular level. On the other hand, the increase in the silica content promoted a subtle decrease in the relaxation times from the composition 99.5 / 0.5 and a more significant decrease for the systems containing 0.75 and 1 wt.% of silica A200. The decrease in the T₁H value indicate increase in the molecular mobility of the systems, pointing change in the crystalline profile of them. This result confirm those found by XRD that showed a progressive decrease in the crystalline organization of PHB A200 systems with increase of silica content (Fig. 1) and by DSC analysis that showed a progressive increase of the population of smaller crystals (Fig. 3). Close inspection of the relaxation values for the R972 hybrids shown in Table 5, permits to observe a progressive increase in the relaxation time with increase in the silica content, from the composition 99.5 / 0.5. This behavior denotes a better dispersion and molecular interaction of the silica in the PHB matrix given its organophilic nature, which provides a more homogeneous dispersion of this nanoparticle compared to A200. This behavior points to the fact that the organophilic silica has dispersed predominantly in the amorphous region of the polymer, a fact consistent with the reduction of the molecular mobility of the material with the increase in the percentage of silica.

CONCLUSION

The addition of silicon dioxide by solution casting method in the PHB matrix induced different changes on the PHB matrix characteristics, depending of the hydrophilic or hydrophobic nature of this nanoparticle. It was observed that silica A200 acted as nucleating agent for PHB, affecting its crystallization kinetics. On the other hand, R972 silica interacted chemically with the matrix, affecting more significantly its crystalline planes. In relation to the degree of crystallinity, it was seen a decrease on this parameter for sample 05A200 among hybrids with hydrophilic silica and for sample 1R972 among hybrids with hydrophobic silica. For studied thermal properties it was not seen important changes for PHB/R972 systems, while PHB/A200 systems presented a progressive increase on the crystallization temperature with increase of A200 concentration. Finally the NMR relaxation results revealed that the PHB/R972 systems presented an interfacial chemical interaction, since T₁H relaxation time values were increased.

This result can be attributed a strong interaction between particle and polymer that restrict the molecular mobility of the systems. In contrary, PHB/A200 systems presented a decrease of T₁H relaxation time values that were consistent with the results provided by other techniques that point to a decrease of crystal size, that results in a bigger molecular mobility. The results obtained from this technique proved that NMR is an effective method for analyzing the action of nanoparticles in the molecular dynamics of nanostructured systems and provide more specific information about interfacial interaction.

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