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RESEARCH ARTICLE

USE OF NMR RELAXOMETRY IN THE EVALUATION OF PHB-BASED HYBRID NANOCOMPOSITE SYSTEMS

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ABSTRACT

Zinc oxide (ZnO) and organophilic Clay (Viscogel B8) were added to poly(3-hydroxid butyrate) (PHB) matrix in some proportions. The nanocomposites containing both nanoparticles were obtained from solution casting method using chloroform as solvent. The films obtained were mainly analyzed by time-domain nuclear magnetic resonance (TD-NMR) to obtain answers about the interactions, dispersion, distribution of nanoparticles and, consequently, the homogeneity of both nanoparticles in the polymer matrix. Combining relaxation data of ^{1}H measured at 23 MHz and from the longitudinal relaxation dispersions measured among 100 KHz to 300 MHz, it was also obtaining information on the influence of both nanoparticles in the polymer characteristics and if there was a synergic effect of ZnO nanoparticle and organoclay, using them together. The results obtained showed that the incorporation of only 0.1% of ZnO caused a great impact in the polymer PHB matrix and in the system obtained.

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INTRODUCTION

Nanocomposite and nanostructured materials are part of a class of hybrid materials, where at least one of its components, has any of the dimensions in the nanometer range up to 100nm *(*Kumar, 2009; Alexandre, 2000; Chandrasekaran, 2013; Galimberti, 2013; Díez-Pascual, 2014; Silva, 2013; Vanderhart, 1996; Vanderhart, 2001; Grunin, 2017; Silva, 2015*)*. These materials have characteristics that distinguish them from the composite mainly due to the higher aspect ratio of the nano-sized particles have, providing a larger surface area. Because of this, the proportions of such fillers are smaller than those used in the production of micrometric producing composite materials with lower density and next resistance of metal materials commonly used *(*Alexandre, 2000; Chandrasekaran, 2013; Galimberti, 2013; Díez-Pascual, 2014; Silva, 2013; Vanderhart, 1996; Vanderhart, 2001; Grunin, 2017; Silva, 2015; Kickelbick, 2017; Silva, 2016; Monteiro, 2012; Soares, 2012; Stejskal, 1994*)*.

The need for multifunctional polymer nanocomposites led to several nanoparticle combinations of different geometries to achieve synergistic effects in the new nanocomposite materials *(*Díez-Pascual, 2014*)*. The obtaining hybrid composites containing more than one type and or nature of nanoparticle has attracted attention of researchers, they have been trying different combinations of nanoparticles, however, the synergistic effect achieved through these combinations are not yet completely understood. It is known that there is an increase of mechanical strength and thermal conductivity, but it is of fundamental importance that the proportion of nanoparticles inserted in the nanomaterial has capabilities to influence in the final materials morphology, which is the most important to obtain new properties increasable *(*Galimberti, 2013; Díez-Pascual, 2014; Silva, 2013; Vanderhart, 1996; Vanderhart, 2001; Grunin, 2017; Silva, 2015; Monteiro, 2012; Soares, 2012; Stejskal, 1994*)*. Several polymers have been used to generate new nanocomposites for different applications. Many researches are attracted from the biopolymers because its biodegradability. In this present study poly (3-hydroxi

butyrate) was chosen as a polymer matrix due its known characteristics and biodegradability (Silva, 2013; Kickelbick, 2017. Knowing that to achieve synergistic effects of two or more nanoparticles depend on the obtaining method of the polymer matrix and nanoparticles involved, as well as the interactions between them and, consequently good dispersion and distribution of them in the polymer matrix. According to this statement, the main objective of this work was two incorporate two distinguish nanoparticles in the PHB matrix to obtain a new material with potential using in film food packing. To achieve the goal of the present work despite traditional techniques solid-state nuclear magnetic resonance (NMR) employing relaxometry as a main alternative technique to evaluate the new materials and especially the effects of nanoparticles in the polymer matrix. Because NMR relaxometry can distinguish the intermolecular interaction, dispersion and distribution of the nanoparticles in the polymer matrix, due to the contribution of the molecular movements and domain formations and components arrangements through the determination of proton spin-lattice relaxation time. This parameter has a time constant T_1H and is sensitive to the changes in the molecular movements according to the changes in the molecular interactions and the chains organizing (Silva, 2015; Kickelbick, 2017; Silva, 2016; Monteiro, 2012; Soares, 2012; Stejskal, 1994; McBrierty, 2006; Tavares, 2018; Aluculesei, 2019). The other interesting relaxometry technique is fast-field cycling (FFC), which promotes a variety of frequency range measuring in a sequence; allowing understand the behavior of the spin populations present in the sample. The frequency decay with the variation of relaxation time shows the sample behavior. According to this statement the main objective of this was the use of nuclear magnetic resonance by relaxometry as a tool for nanocomposite evaluation to obtain responses on the interaction, dispersion, distribution and homogeneity of the system constituents.

Experimental

Systems Preparation: Nanocomposites were prepared in solution using chloroform as solvent. The ratios used for organoclay Viscogel B8 (B8) were 1, 3 and 5 wt% of and three different ratios of zinc oxide (ZnO), 0.1 %, 0.25 % and 0.5 % by mass were employed for each organoclay percentage. The total mass used to produce each film was 5 g and the solutions were prepared at a concentration of 10 %. Different proportions of nanoparticles were dispersed in chloroform with the aid of ultrasound and were then added to the polymer already solubilized. The mixtures were kept under stirring for 24 hours and then poured into petri dishes. Drying of the solvent was carried out at room temperature and their elimination was accompanied by the mass variation of the film until its stabilization. After that the infrared spectroscopy was also done to confirm the solvent elimination.

Low-field NMR: The relaxation time was analyzed in a Maran Ultra *(Oxford Instruments®)* low-field NMR spectrometer, using an 18 mm NMR tube, operating at 23 MHz for the hydrogen nucleus. The pulse sequence used to determine the spin-lattice relaxation time data was inversion-recovery (recycle delay - 180° - τ- 90° - acquisition data) and the 90° pulse of 4.7μs was calibrated automatically by the software of the instrument. The amplitude of the FID was sampled for 20 τ data points, ranging from 0.01 to 5000 ms, using 40 data points and 4 scans for each point. The same sample was analyzed at 30 ± 2 °C.

The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the *WINFIT®* (2.4) software. Distributed exponential fits by plotting the relaxation amplitude versus relaxation time were performed using the *WINDXP®* (1.8.1) software. Both programs come with the low-field NMR spectrometer. Measurements for frequencies between 100 kHz and 9 MHz were made using a home made Fast Field-Cycling NMR relaxometer, with a recycle time $5T_1$ and the polarization time was 5s. These measurements allowed us to evaluate the behavior decay of spin-lattice relaxation decay. A Bruker magnet BE-30 and an Avance II NMR console were used to obtain the T_1 values between 9 MHz and 90 MHz. And measurements at 300 MHz were obtained using a 7 T superconductor magnet. The conditions applied was the same used in others works (Tavares, 2018; Aluculesei, 2019.

RESULTS AND DISCUSSION

The values of T_1H at 23 MHz for all system evaluated are shown in Table 1.

Table 1. T_1H Relaxation values of PHB/B8/ZnO nanocomposites

%B8	%ZnO	T_1H (ms) ± 2%
0	0	654
1	0	658
3	0	609
5	0	567
0	0.10	584
0	0.25	574
0	0.50	554
1	0.10	649
1	0.25	621
1	0.50	651
3	0.10	624
3	0.25	608
3	0.50	594
5	0.10	540
5	0.25	510
5	0.50	532

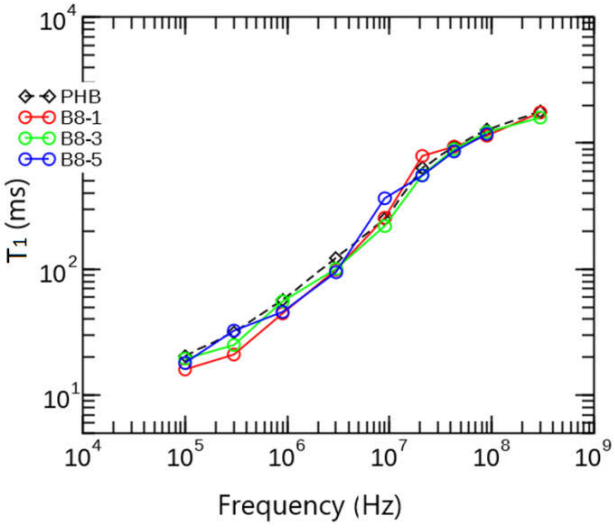

Figure 1. Comparative tendency graphics of the relaxation behavior versus frequency for PHB containing only Viscogel B8

According to these results it is first observed a significant change in the T_1H values for the systems containing ZnO nanoparticles, even in the proportions with small amounts of ZnO nanoparticles (0.1%), comparing to the value of the pure polymer.

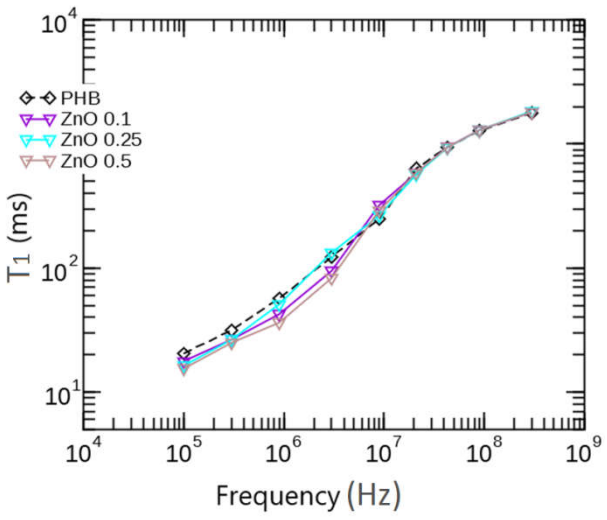

Figure 2. Comparative tendency graphics of the relaxation behavior versus frequency for PHB containing only ZnO

This indicates a pronounced effect of the ZnO nanoparticles in the polymer matrix, due to the dispersion/diffusion of these particles in the molecular chain, according to the collective movements. This behavior was detected, even when these particles are incorporated in the isolated form and together with organoclay for the samples containing 3 and 5% in the polymer matrix. For these cases there was a decrease in the relaxation values due to the fact that new intermolecular interaction among the molecules components in the systems is good and can promote good dispersion and also distribution of these nanoparticles in the PHB matrix in an efficient manner. This decrease in T_1H values for the systems containing only zinc oxide indicates an increase in the polymer chains molecular mobility, which may occur due to a decrease in the degree of crystallinity promoted by the good intermolecular interaction, and/or due to paramagnetic effect of ZnO, which causes a decrease of the hydrogen relaxing near to them, which confirms the molecular arrangement of the polymer molecules around ZnO particles, which may promote a formation of specific morphologies between these nanoparticles and polymer chains. The molecular size of zinc oxide, around 75 nm, my also interfere in the PHB crystallization process. As the NMR relaxometry is a technique that observes the sample as a whole and it is possible to measure the averages of the relaxation values of all hydrogen populations presents in the material. Evaluating the samples containing both clay and zinc oxide, the occurrence of more intercalated morphology of the clay lamellae results in an increase in the T_1H value, due to the decrease in the chains molecular mobility. Another important aspect is observed through T_1H data, which is the occurrence of a synergistic effect when adding two nanoparticles together. It is noted that the material obtained after incorporation any quantity of ZnO, together with each clay proportion, showed a decrease in the values of relaxation, especially for the systems containing 5%of clay. This occurs because the presence of the zinc oxide that may have been able to change the way of clay is dispersed in the polymer matrix and consequently altering the molecular mobility of the chains, due to the changes in the systems morphology and or arrangements, since new interactions have been created between nanoparticles and polymer matrix.

To better evaluate the behavior of the samples through the proton spin-lattice relaxation time determined by fast-field cycling measurements, it is possible to use the decay curves of relaxation time versus frequency range of the proton nuclei for each type of sample. Figures to 1 from 5 show the graphics of comparative tendency of relaxation time versus frequency behavior for the samples based on PHB and the nanoparticles systems. Analyzing the decay of each system curves one can see that there is a spread of the curves at the end of the decay, in the region of low frequencies, this region belongs to the amorphous region, indicating that the clay is preference being dispersed in this region. Evaluating the systems containing only zinc oxide (Fig.2) there was not seen significant changes or spread in the curves decay, only a small spread for 0,1 and 0.5% of ZnO, showing that this nanoparticle is dispersed in the same manner, homogeneously, in the matrix. Therefore, analyzing the hybrid system containing 1% (Figure 3) and 3% (Figure 4) of clay and different proportions of ZnO, there was a spread of the T_1 decay observed in low frequencies indicating that the nanoparticles are predominant dispersed in the amorphous regions. These behaviors are due to the changes in the collective molecular movements in the system and the formation of multiples intermolecular interaction that promotes changes in the systems arrangements and morphology.

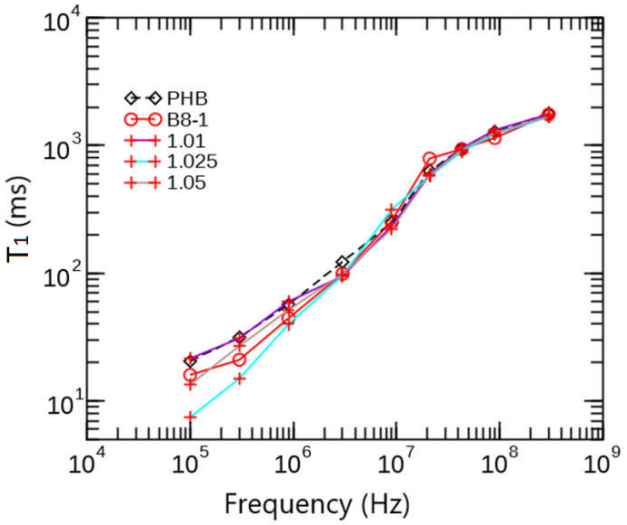

Figure 3. Comparative tendency graphics of the relaxation behavior versus frequency for PHB and the hybrid materials of PHB/B8/ZnO with 1% of B8

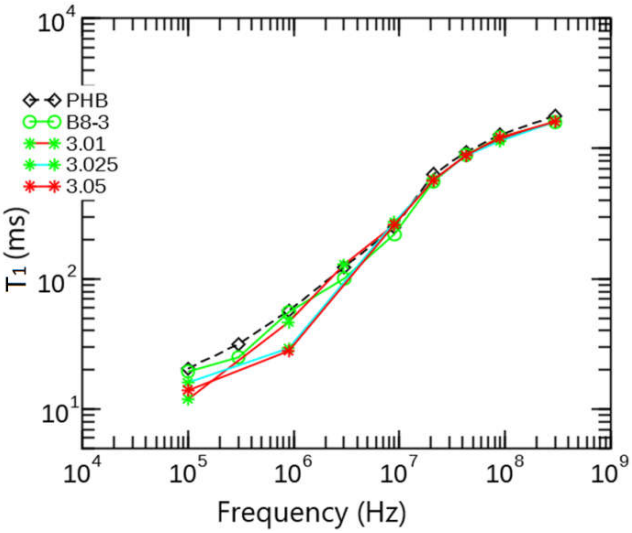

Figure 4. Comparative tendency graphics of the relaxation behavior versus frequency for PHB and the hybrid materials of PHB/B8/ZnO with 3% of B8

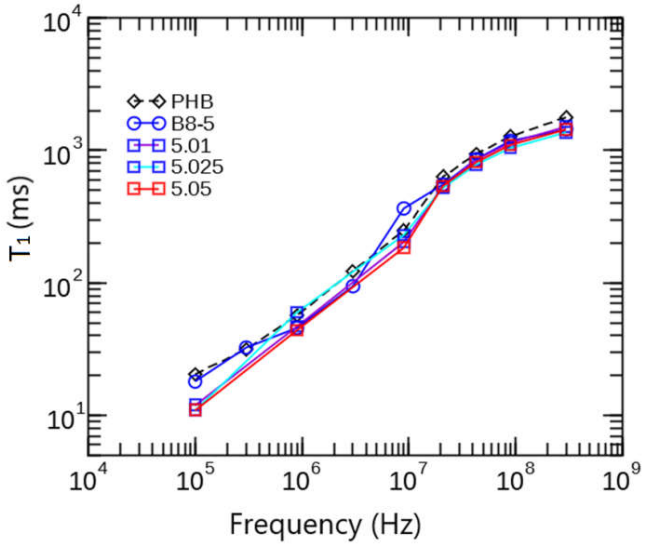

Figure 5. Comparative tendency graphics of the relaxation behavior versus frequency for PHB and the hybrid materials of PHB/B8/ZnO with 5% of B8

Finally, analyzing the systems containing 5% of clay and ZnO proportions a distinct behavior was found. There was a spread in the low frequencies as was already observed for the other proportions, but a small spread in the high frequencies (rigid part of the systems, including crystalline region) was also observed. This behavior comes from the fact that in this proportion there was a synergic effect of the zinc oxide and the clay, because the zinc oxide promotes a better dispersion of the clay in both regions of frequencies, indicate that the nanoparticles are dispersed and distributed in the rigid and amorphous regions. The decrease in the values of relaxation data more expressive in this proportion indicates that ZnO promotes a better clay exfoliation, because this nanoparticle is near to the hydrogens of the polymer matrix acting as a relaxing agent (similar behavior was found for Wanderhat, 2001; Silva and Tavares, 2015 and Silva et al., 2016). Thus, the nanoparticles are well dispersed and distributed along with the matrix, promoting changes in the clay morphology and arrangements due to the new multiple intermolecular interactions.

Conclusion

The obtaining PHB nanocomposites containing two nanoparticles, ZnO and organoclay was possible through the solution method. The XRD analysis showed that there was increased crystallinity of the materials containing both nanoparticles due to performance of these as nucleating agents for the material. The evaluation of these nanocomposites by low-field NMR was able to provide valuable information regarding the interaction of the nanoparticles with two PHB, besides being able to indicate on the distribution and dispersion of these nanoparticles in the polymer matrix. What we found then was a decrease in the mobility of the polymer chains, observed by increasing the value of T_1H, due to the predominantly interspersed morphology training with the lamellae of clay and the occurrence of close interactions between the PHB and ZnO. From the results one cam conclude that there is a strong indication of a generation of synergic effect when both nanoparticles are added together, due to the multiples intermolecular interactions.

The zinc oxide facilitates the dispersion of the clay, promoting morphology with a predominance of exfoliated one. It is also possible to infer that changes may promote new characteristics in the hybrid materials.

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