

## Evaluation of PHB/Clay Nanocomposite by Spin-Lattice Relaxation Time

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Poly(3-hydroxybutyrate) (PHB) based on nanocomposites containing different amounts of a commercial organically modified clay (viscogel B7) were prepared employing solution intercalation method. Three solvents, such as:  $\text{CHCl}_3$ , dimethylchloride (DMC) and tetrahydrofuran (THF) were used. The relationship among the processing conditions; molecular structure and intermolecular interaction, between both nanocomposite components, were investigated using a nuclear magnetic resonance (NMR), as a part of characterization methodology, which has been used by Tavares et al. It involves the hydrogen spin-lattice relaxation time,  $T_{1H}$ , by solid state nuclear magnetic resonance, employing low field NMR. X ray diffraction was also employed because it is a conventional technique, generally used to obtain the first information on nanocomposite formation. Changes in PHB crystallinity were observed after the organophilic nanoclay had been incorporated in the polymer matrix. These changes, in the microstructure, were detected by the variation of hydrogen nuclear relaxation time values and by X ray, which showed an increase in the clay interlamellar space due to the intercalation of the polymer in the clay between lamellae. It was also observed, for both techniques, that the solvents affect directly the organization of the crystalline region, promoting a better intercalation, considering that they behave like a plasticizer.

**Keywords:** NMR, PHB, Nanocomposite

### 1. Introduction

Biodegradable polymers have been focused on many studies, due to the fact that the study of these polymers is a topic of high interest because of the great quantity of wasted polymers in the world. The development of biodegradable materials with controlled properties has been widely studied. PHB is one of the most studied biodegradable polymers used to substitute synthetic plastics in their application that causes an environmental impact, such as food packaging. Therefore, the use of biodegradable polymers is limited due to its characteristics such as molecular weight; structural crystallinity and amorphous phase, as well as its narrow range of processing temperature<sup>1,2</sup>; these characteristics promote bad mechanical properties. According to these statements some modifications in the chemical structure of these biopolymers can be done. Copolymerization with valerate generates a poly-b-(hydroxybutyrate-co-valerate) (PHB-HV), which is one way to improve the PHB mechanical properties. PHB-HV is less stiff and tougher than PHB and because of this the copolymer is used as packaging material. Then, the generation of nanocomposite based on the biodegradable polymers has been considered one of the best routes to improve the mechanical properties of PHB<sup>3,4</sup>.

The preparation of hybrid nanocomposite, employing inorganic nanofiller, such as montmorillonite and/or other type of organically modified clay, has a great industrial interest to produce biodegradable nanocomposites that has its crystallinity reduced; gas and water vapor barrier increased; as well as an increase in the thermal stability<sup>3,5</sup>.

To accompany these studies some conventional techniques, such as thermal analyzes, X ray diffraction and transmission electronic microscopy (TEM) are normally used. Therefore, one of the best spectroscopy that has been initiated in these studies is nuclear magnetic resonance, which is able to evaluate the polymer samples

in solution and solid state<sup>5-8</sup>. The solid state techniques can include the hydrogen nuclear relaxation measurements, which will give response on the molecular dynamic of the hybrid compound and it also evaluates the nanoparticle dispersion in the polymer matrix<sup>3,4,9,10</sup>. The hydrogen relaxation times<sup>9,10,13,14</sup> can be measured directly in a low field NMR and it gives response on the nanoparticle dispersion; interaction between both nanocomposite components and better processing conditions<sup>9,10</sup>.

In this work nanocomposites based on PHB, containing 1, 3 and 5 wt. (%) of commercial organo-modified montmorillonite clay (viscogel B7 – which is intercalated with C-12) were prepared by solution intercalation reaction and they were characterized using a methodology (developed in our laboratory<sup>9-10</sup>), which involves the determination of hydrogen spin-lattice relaxation time, by nuclear magnetic resonance, and the use of conventional X ray diffraction to measure the basal space of nanoclay. Both techniques used give information that is complementary, because they are measured in different time scale.

In this work we have decided not to use transmission electronic microscopy (TEM), due to the fact that the micrographs do not represent the median behavior of the sample, as NMR do. Besides the quantity of sample analyzed by TEM is very small and it is not representative comparing to 5 g used in the NMR measurements.

### 2. Experimental

The nanocomposites were prepared by solution intercalation reaction, which is a non aggressive method, using  $\text{CHCl}_3$ , dimethylchloride (DMC) and tetrahydrofuran (THF) as solvents. These sol-

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vents were chosen according to their solubility obtained by previous study in PHB. The solutions of PHB and organoclay were prepared isolated to obtain the polymer/clay ratios 99/1, 97/3 and 95/5 percentage of clay in the polymer matrix. The isolated solutions were kept in the agitation for 24 hours at room temperature. After that, the solutions were mixed and left for 24 hours being stirred. At the end of this time the solutions were casting on the plates and were kept at room temperature. These conditions were careful chosen, taking into consideration that PHB is a biodegradable polymer with singular properties and characteristics.

X ray diffraction (XRD) analyses were done in a Rigaku D/max 2400 diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation of wavelength  $1.542 \text{ \AA}$ , at room temperature scanning over angle ( $2\theta$ ) range from  $2^\circ$  to  $20^\circ$  in  $0.02$  steps, at a scanning rate of  $8^\circ/\text{min}$ .

Low field NMR spectrometer, MARAN ultra 23 (Resonance - Oxford - UK), operating at 23 MHz (for hydrogens) and equipped with an 18 mm variable temperature probe, was used for the hydrogen relaxation measurements. Hydrogen spin-lattice relaxation times were determined directly by the traditional inversion-recovery pulse sequence (recycle delay -  $180^\circ$  -  $\tau$  -  $90^\circ$  - acquisition), the  $90^\circ$  pulse,  $4.6 \mu\text{s}$ , was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty  $\tau$  data points, ranging from 0.1 to 5000 ms, with 4 scans each and 5 seconds of recycle delay. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the WINFIT (program supplied from the Resonance).

### 3. Results and Discussion

The casting films of the nanocomposites, prepared in different solvents (DMC, THF and  $\text{CHCl}_3$ ), were analyzed by X ray diffraction and the profiles obtained for each nanocomposite are shown in Figures from 1 to 3, respectively.

The disappearance of the main peak of the clay, which shows the intensity of lamellae organization (at  $2\theta$ ), can be attributed to the nanocomposites formation. Although, for the nanocomposites prepared in THF, the referring peak of the clay did not disappear completely, this can indicate that this is not a good solvent for this system. Comparing widths of the half height of the nanocomposites prepared in DMC and chloroform, one concludes that both solvents are good for the preparation of nanocomposites PHB/clay, due to the intercalation/exfoliation formation. One can observe that the decreasing in the peaks intensity is an indication of the increase in the exfoliation process, especially when 5% of nanoclay was incorporated. However, a non similar behavior was found for the nanocomposites prepared in THF, which can be attributed to a no good solubilization/interaction of the system in this solvent. Knowing that the X ray scale is not enough to obtain more information than it was explored, we have decided to use solid state NMR, which is more sensitive and permits to evaluate the median behavior of the sample, because the time scale of the measurement is at the molecular level and the domains detected have sizes, which vary from 25 to 50 nm.

According to the main purpose of this work, hydrogen spin-lattice relaxation time measurements were recorded to get more information on samples homogeneity; clay dispersion and interaction process in the nanocomposite. The relaxation data measured from one fit exponential are listed in the Table 1.

The evaluation of the relaxation data obtained from the one fit exponential reveals the major contribution of the domain that controls the relaxation process. In solids the hydrogen spin-lattice relaxation is controlled by the dipolar intermolecular interaction process. From Table 1 the results showed that DMC was a better solvent for the inter-

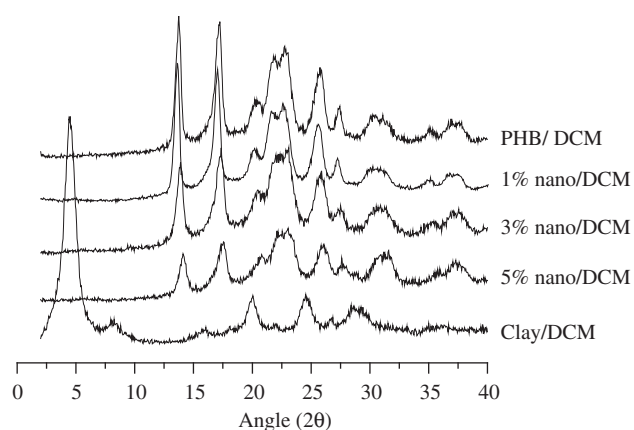


Figure 1. X ray diffraction of the nanocomposites prepared in DMC.

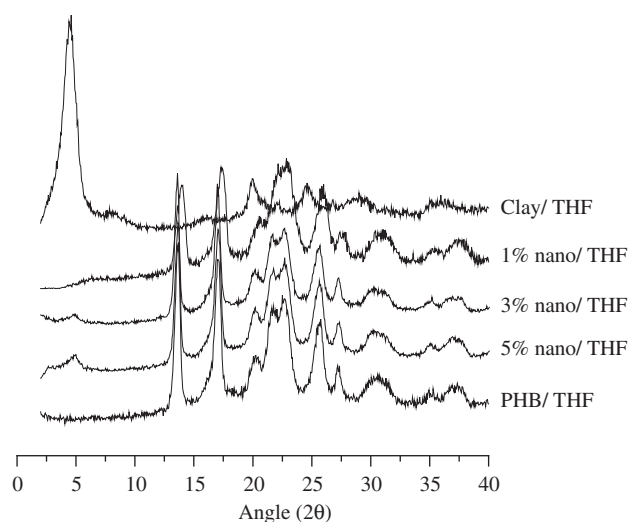


Figure 2. X ray diffraction of the nanocomposites prepared in THF.

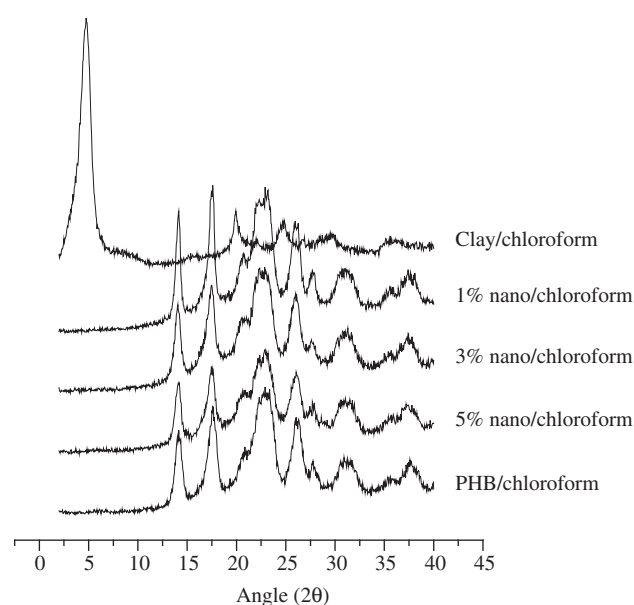


Figure 3. X ray diffraction of the nanocomposites prepared in  $\text{CHCl}_3$ .

**Table 1.**  $T_{1H}$ , obtained with one fit data for the nanocomposites.

Sample	$T_{1H_{onefit}}$ (ms)
PHB (DMC)	600
PHB/clay 1% (DMC)	456
PHB/clay 3% (DMC)	451
PHB/clay 5% (DMC)	500
PHB (THF)	513
PHB/clay 1% (THF)	471
PHB/clay 3% (THF)	459
PHB/clay 5% (THF)	500
PHB (CHCl <sub>3</sub> )	563
PHB/clay 1% (CHCl <sub>3</sub> )	451
PHB/clay 3% (CHCl <sub>3</sub> )	474
PHB/clay 5% (CHCl <sub>3</sub> )	441

calation/exfoliation process. First of all the difference from the PHB relaxation value and the values determined for the nanocomposite is higher than the other two solvents, showing that in DMC a good solubilization of both nanocomposite components was found. Another point is related to the fact that no difference between  $T_{1H}$  values was found for 1 and 3% of nanoclay incorporated in the PHB matrix. This fact can indicate that the clay had a very good dispersion and a good exfoliated/intercalated nanocomposite ratio was also found. Besides this, a pronounced change, which is an increase in the relaxation data, was detected when 5% of nanoclay was incorporated in relation to the value of PHB in this solvent. This can be explained as an increase in the intercalation, because an exfoliation process causes a decrease in the value of hydrogen relaxation time, comparing to the initial polymer, since the polymer chains are around the lamellae, and the metals present in the lamellae promote a decreasing in the relaxation time of the nucleus near them. However, an increase in the hydrogen relaxation when 5% of nanoclay was introduced indicates that more intercalated nanocomposite was formed, because the intercalation process restricts the polymer chains molecular mobility, which is reflected in the hydrogen relaxation value. According to the data both 1 and 3% of nanoclay were very well dispersed in DMC solvent.

Analyzing the hydrogen relaxation data for the nanocomposite prepared through THF, one can see that for both 1 and 3% of nanoclay there was a decrease in the relaxation values, less pronounced than for DCM, and the same numeric value of relaxation was found for 5% of nanoclay. However, the difference between the value of relaxation for PHB and nanocomposite with 5% is practically zero, which is an indication that this quantity of nanoclay was not good dispersed and no interaction between the nanocomposite components was found for this ratio. These results confirm the morphological behavior found by X ray diffraction, for the 5% of nanoclay, the peak in  $2\theta$  is still there. In THF 5% of nanoclay was not well dispersed and no PHB nanocomposite was formed. According to the relaxation results both 1 and 3% of nanoclay were better dispersed in solvent, but 3% of its behavior was a little better.

Evaluating the nanocomposites obtained by chloroform, for all nanoclay ratios, there was a decrease in the relaxation values and no significant change was observed in the values of hydrogen relaxation time for all nanoclay ratios, comparing to PHB. This fact is an indication that this solvent also promotes an intercalation and/or exfoliation, due to the similarity in the relaxation parameter which comes from

the fact that CHCl<sub>3</sub> promotes a different organization of the nanocomposite that is independent from nanoclay ratio. This particularity can be attributed to the interaction forces of the solvent solubilization. Analyzing the hydrogen relaxation value for 5% of nanoclay, it can be concluded that it is a better ratio for this solvent.

#### 4. Conclusions

According to the results, one can conclude that the methodology employed was efficient, rapid and practical to better understand the behavior of the nanocomposites formed by PHB/nanoclay. Both X ray and relaxation time techniques were complementary. The NMR relaxation data informed about the nanoclay dispersion; interaction; nanocomposite structure organization, and also inferred about the better nanoclay ratio for each solvent.

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