The Evaluation Polymeric Nanocomposites from Nuclear Magnetic Resonance Relaxometry

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Abstract— **Solid-state Nuclear Magnetic Resonance (NMR) has many techniques that include hydrogen nuclear relaxation times, such as: spin-lattice relaxation time in the laboratory frame (T_1H) and spin-lattice relaxation in the rotating frame ($T_1\rho H$). These relaxation parameters involve changes in thermal equilibrium of spin systems and the hydrogen relaxation times can be measured directly, using low-field NMR. The efficiency of the process can be correlated with the structure and the value is intrinsically related to the system's morphology; consequently, the relaxation times can be used to evaluate the nanoparticles' dispersion in the polymer matrix; the interaction between both nanocomposite components; the molecular dynamic of the hybrid compounds and also the molecular domains formation in an organic material. This feature makes these techniques good tool to analyze the molecular dynamics of polymer systems, as well as the nanocomposites. In this work, we want to show the evaluation of polymeric nanocomposites formation employing the determination of proton spin-lattice relaxation time, using low-field nuclear magnetic resonance. The nanocomposites were mainly characterized by solid state nuclear magnetic resonance relaxometry through the determination of proton spin-lattice relaxation time. The determination of this parameter was carried out to evaluate the organoclay exfoliation and intercalation process in the polymeric matrix, for samples using organoclay as a nanoparticle, as well as the dispersion and distribution of them along the macromolecular chains; this parameter was also used to detect the dispersion and distribution of the spherical and tubular nanoparticles in the polymeric matrix. The proton NMR relaxation data showed that the polymeric nanomaterials investigated presented good nanoparticle dispersion and the distribution, as well as the intermolecular interactions between hybrids components.**

Keywords - polymeric nanocomposites; nanoparticles; rexalation times; nuclear magnetic resonance

I. INTRODUCTION

The solid-state nuclear magnetic resonance [1] is a spectroscopy that comprehends many techniques, one of them is the hydrogen nuclear relaxation times, such as: spin-lattice relaxation time in the laboratory frame, promotes evaluation of the samples in the MHz scale and spin-lattice relaxation in the rotating frame is sensitive to the movements in the tens of kilohertz [1-3]. Both relaxation parameters involve changes in thermal equilibrium of spin systems and the responses of them are intrinsically related to the system's molecular dynamic that is derived from the morphology [4-6]. Consequently, the relaxation measurements can be used to evaluate the nanoparticles' dispersion in the polymer matrix, the interaction between both nanocomposite components, the molecular dynamic of the hybrid compound and also the molecular domains formation in an organic material [7-9]. This feature makes these techniques a good tool to analyze the molecular dynamics of polymer systems, as well as the nanocomposites [8-11].

In this work, we want to show the evaluation of polymer nanocomposites employing proton spin-lattice relaxation time, using the proton relaxation parameter employing low-field nuclear magnetic resonance.

This work will present the evaluation of different nanostructured materials based on synthetic and biopolymers as well distinct nanoparticles by the use of nuclear magnetic resonance relaxometry to obtain responses on the intermolecular interactions and the dispersion and distribution of the nanoparticles in the polymer matrix

II. EXPERIMENTAL

A. *NMR relaxation measurements*

The relaxation time was analyzed in a MARAN Ultra low-field NMR (LF-NMR) spectrometer (Oxford Instruments, Oxford, UK), using an 18 mm NMR tube, operating at 23 MHz for the hydrogen nucleus. The pulse sequence used to obtain the spin lattice relaxation time data was inversion-recovery (recycle delay - 180° - τ - 90° - acquisition data) and the 90° pulse of 4.5μs was calibrated automatically by the instrument's software. The amplitude of the FID was sampled for twenty 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 27 ºC. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the WINFIT program. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the WINDXP software. Both WINFIT and

WINDXP are commercial programs and come with the low-field NMR spectrometer.

All solid-state NMR spectra were obtained on a VARIAN spectrometer, UNIT-Plus, 9.4 Tesla, operating at 104 MHz for ^{13}C nuclei and 79.49 MHz ^{29}Si. The samples were packed in a 7mm zirconia rotor that was spun in the magic angle at about 6 kHz for the carbons-13 nucleus. The ^{13}C cross polarization magic angle spinning (CPMAS) were first done to obtain the conditions to apply the variable contact time experiment (VCT), which were carried out using 2 s of recycle delay with the increase of contact-times varying from 100 to 8000μs, the hydrogen decoupling field strength was 40 KHz. From this experiment it was also determined the values of proton spin-lattice relaxation time in the rotating frame ($T_1\rho H$), which is indirectly determined from the intensity decay of each resolved carbon. Hexamethyl benzene (HMB) was used as external standard; the methyl carbons were assigned as 17.3 ppm.

III. RESULTS AND DISCUSSION

A. Evaluation of PHB-organoclay systems obtained by solution

Low-field NMR analyses were used to determine the proton spin-lattice relaxation time for the PHB/viscogel B8 nanocomposites. Table I shows the proton T_1 relaxation values of the PHB/viscogel B8 nanocomposites, the nanostructure materials were obtained through intercalation solution method.

TABLE I. HYDROGEN NUCLEAR RELAXATION VALUES FOR THE NANOCOMPOSITES OF PHB/VISCOGEL B8

PHB/Viscogel B8	**T_1H (ms)**
0/100	683
99/1	654
97/3	570
95/5	**440**
93/7	489
90/10	487

A decreased in the proton relaxation value with the increased of organoclay comes from the exfoliation process that occurs predominantly comparing to intercalation process. This statement is confirmed by the presence of metals in the clay lamellae that are agent that promotes the proton relaxing acceleration as the polymer chains are around the clay lamellae, confirming the for changes occurred the in polymer and clay structures after a polymeric nanocomposite being formed. Up to 5% a decreased in the T_1H is due to the exfoliation process, after this proportion the values are still lower than the polymer matrix, due to the same effect, but they began to increase, because some intercalation process is being done due to the large amount of organoclay to be exfoliated, dispersed and distribution in the polymer matrix.

The proton NMR relaxation data showed that the polymer nanomaterials investigated presented good nanoclay dispersion in the polymeric matrix, promoting a formation of mixed nanocomposite structure containing part exfoliated and part intercalated.

B. Evaluation of HIPS-organoclay systems obtained by solution

The nanocomposites obtained were mainly characterized by solid state nuclear magnetic resonance relaxometry, through T_1H measurements. The determination of proton spin-lattice relaxation time was carried out to evaluate the clay exfoliation and intercalation. The relaxation determination was done in a low-field NMR spectrometer. Tables II and III show the T_1H data for the polymer system containing S4 and S7, respectively, as nanoparticles. S4 contains Bis (Hydrogenated Tallow Alkyl) Dimethyl Ammonium (BHTADMA) as a surfactant and S7 contains Dimethyl Benzil Hydrogenated Tallow Ammonium (DMBHTA) as a surfactant.

TABLE II. PROTON SPIN-LATTICE RELAXATION FOR HIPS AND THEIR NANOCOMPOSITES WITH S4

Samples	**T_1H (ms)**
HIPS	504
HIPS41	483
HIPS42	**463**
HIPS43	479
HIPS45	507

TABLE III. PROTON SPIN-LATTICE RELAXATION FOR HIPS AND THEIR NANOCOMPOSITES WITH S7

Samples	**T_1H (ms)**
HIPS	504
HIPS71	503
HIPS72	**434**
HIPS73	468
HIPS75	449

According to the relaxation time values listed in both Tables II and III, independently of organoclay type used, the best quantity of nanoparticle to be well dispersed and distributed in the polymer matrix was 2%, in this proportion higher degree of exfoliation process occurred, due to the decrease in the relaxation time, because of the relaxing effect of the paramagnetic metal present in the clay structure. These metals influence direct in the protons relaxation decreasing it, which confirms the exfoliation process.

C. *Evaluation of PLA-silica systems obtained by solution*

Two silica types A200 (hydrophilic) and R972 (hydrophobic) were incorporated in the PLLA matrix [11] and both silica types caused changes in T_1H values due to the changes in the molecular mobility, as a consequence of nanoparticle dispersion and distribution in the polymer matrix. Table IV shows the T_1H values for the PLLA (pellet), 5% PLLA and their nanocomposites with A200 and R972 silica.

TABLE IV. T_1H VALUES FOR THE PLLA (PELLET), 5% PLLA AND THEIR NANOCOMPOSITES WITH A200 AND R972 SILICA.

Sample	**T_1H**
5% PLLA	630
5% PLLA + 0.5 mg A200	657
5% PLLA + 1mg A200	671
5% PLLA – 0.5mg R972	681
5% PLLA - 1mg R972	660

The effects of 0.5mg of both silica type A200 and R972 were comparable. However, comparing the addition of the samples with 1mg of A200 or R972, the effect of this quantity of silica in the system containing A200 was stronger than the system with 1mg of R972.

For film formed from 5% PLLA an increase in the quantity of R972 decreased the T_1H, which is derived from the dispersion of the silica, this system has an opposite behavior compared to A200 addition.

Therefore, both silica types had promoted changes in the relaxation time as a consequence of silica dispersion and distribution in the polymer matrix. This confirms that the relaxation time parameter was effective to show the effect of nanoparticles with spherical form, such as silica.

D. *Evaluation of EVA-silica systems obtained by melting processing*

The evaluation of EVA-silica system was evaluated by the determination of proton spin-lattice relaxation time in the rotating frame, $T_1\rho H$, it was determined through the decay of the resolved carbons with the increasing of the contact-times, obtained during the VCT experiment. The values of this parameter are listed in Table V.

TABLE V. $T_1\rho H$ VALUES FOR EVA AND THE MEMBRANES WITH SiO_2 5% AND SiO_2 20%, FOR THE CARBON LOCATED AT 34 PPM (CH_2 FROM EVA MATRIX)

Samples	**$T_1\rho H$ (ms)** **34 ppm**
EVA	2
EVA/SiO_2 5%	**1**
EVA/SiO_2 20%	2

The decrease of 50% in the $T_1\rho H$ value for the EVA chains in the EVA/SiO_2 5% nanocomposite shows that the EVA chains are interacting intimately with SiO_2, as a consequence of the silica oxide has being well dispersed and distributed in the polymer matrix, which causes a decreases in the $T_1\rho H$ parameter due to the decrease in the spatial proximity, promoting a strong intermolecular interaction. Analyzing the EVA/SiO_2 20% $T_1\rho H$ value, no change in the parameter value was found comparing to EVA itself, indicating an occurrence of phase separation, because the quantity of silica is high to be well dispersed and distributed in the polymer matrix, as a consequence an agglomeration of silica particles occurs.

E *Evaluation of EVA-carbon nanotubes system obtained by solution method*

The relaxation parameter was also used to evaluate the polymer nanocomposite when the nanoparticle has a tubular form, such as carbon nanotubes.

Table VI shows the proton spin-lattice relaxation time evolution of EVA-carbon nanotubes modified with carboxylic acid system, varying the proportion of carbon nanotubes; these systems were prepared by solution dispersion method.

TABLE VI. PROTON SPIN-LATTICE RELAXATION TIME FOR EVA-CARBON NANOTUBES SYSTEMS

Samples	**CNT (% w/w)**	**T_1H (MS)**
EVA	0.00	60
EVA/NTC001	0.01	57
EVA/NTC010	0.10	56
EVA/NTC100	1.00	57

According to the relaxation data, the addition of small quantity of carbon nanotubes modified with acid does not influence sufficiently the molecular dynamic of the EVA matrix, the very low decreased in the relaxation value could be associated to some dispersion/distribution of the CNT in the EVA matrix.

These systems were also evaluated by the domain distribution curves (Figure 1). The distribution curves show some displacement for the systems that contains 0.1 % w/w of modified carbon nanotubes, which is in accordance with the relaxation data observed in the Table VI.

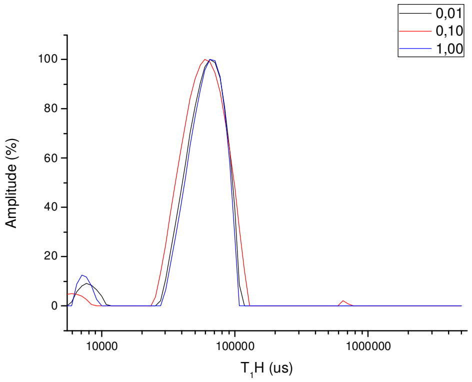

Figure 1. Domain distribution curves determined for the nanomaterials formed by EVA and modified carbon nanotubes.

IV. CONCLUSIONS

According to the relaxation data presented for the systems that using biopolymer and distinct nanoparticles we can see that independently of nanoparticles form their dispersion and distribution in the polymer matrix, as well as the intermolecular interaction can be accompanied by the proton spin-lattice relaxation time values.

For the EVA systems the nanostructured materials formed present a good nanoparticle dispersion and distribution, as a consequence of the preparation mode and the polymer matrix nanoparticle pair.

The evaluation of polymer nanomaterials was clearly obtained according to the changes in the relaxation time values comparing to the polymer matrix before the nanoparticles being incorporated to them. The NMR data showed to be a good alternative technique to be used to evaluate these type of materials.

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