Carbon-13 Solid State NMR Techniques to Evaluate the Morphology of PP/TiO$_2$ Composites

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Abstract

Solid state NMR was successfully used to determine the proton spin-lattice relaxation time in the rotating frame (T$_1\rho$H) for systems based on polypropylene (PP) and PP with titanium dioxide (TiO$_2$) organically modified or unmodified incorporated, in order to understand the molecular behavior of these systems. These techniques were employed in the samples organically modified and unmodified TiO$_2$ to investigate the effect of organic modification on the dispersion and distribution of the particles in the PP matrix. The results were analyzed in terms of the effect of the particles organic modified or not according to the intermolecular interaction in the composites. According to the T$_1\rho$H values, all composites showed at least two domains: the short values were related to the rigid part, which included the crystalline and amorphous phase constricted in it, while the longer times were attributed to the amorphous region, which had higher molecular mobility compared to the rigid region of the materials. The increase in the relaxation time parameter in the composites compared to the pure PP was associated to the strong interaction between titanium dioxide particles and the polymer chains. This effect was more pronounced for the systems containing organically modified TiO$_2$. According to the results, it could be inferred that intermolecular interaction occurred in the CH$_2$ and CH groups, being more intense with CH$_2$ groups. Finally, the solid state NMR techniques were able to evaluate the molecular dynamics of those systems.

Keywords

1. Introduction

Solid-state nuclear magnetic resonance is a non-destructive spectroscopy and it comprises many techniques and also permits us to analyze several nucleuses that contain different information on materials, especially polymer and their derivative materials [1]-[5]. Carbon-13 is an important nucleus that gives many responses on polymer chemical structure, arrangements, configurational and is specific to evaluate the molecular dynamics of polymers and materials based on it [6]-[11]. According to this statement, in this work, we have chosen to use the solid-state carbon-13 NMR spectroscopy as a tool to evaluate the systems formed by PP and titanium oxide modified or not, in order to obtain response on the molecular interaction between polymer and particles and also the way that the particles are dispersed and distributed.

The combination of solid state carbon-13 NMR techniques such as: magic angle (^{13}C MAS); spinning cross polarization magic angle spinning (^{13}C CPMAS) and variable contact time (VCT) together with the measurement of proton spin-lattice relaxation time in the rotating frame, with a time constant $T_1\rho$, will give many important information on polymer systems about intermolecular interactions and particles dispersion and distribution. The spin-lattice relaxation in the rotating frame can be determined through the decay of the resolved carbons during the variable contact time experiment under spin-lock conditions that generate a rotating magnetic field near the resonant frequency perpendicular to the static magnetic field [12]-[18].

The hydrogen MAS also is an important technique to help the evaluation of chains molecular dynamics and together with the carbon-13 NMR responses allow to understand the behavior of polymer systems [19] [20].

The first objective of this work is preparing PP/TiO$_2$ composites and nanocomposites using TiO$_2$ with or without organic surface modification with hexylamine, seeking materials with characteristics of photodegradation or photostabilization. The second main objective is to use the combination of solid-state nuclear magnetic resonance techniques as a tool to evaluate the PP/TiO$_2$ systems, in their forms, according to the particles dispersion, distribution and their influence on polymer systems organization and morphology.

2. Experimental

2.1. Sample Preparations

The PP/TiO$_2$ composites and nanocomposites were initially prepared by physical mixing of the polymer and particles in a Tepron mixer at a rotation speed of 5 rpm for 30 min, using different TiO$_2$ particle concentrations: 0.25% (w/w), 0.50% (w/w), 0.75% (w/w), 1.0% (w/w). Modified and unmodified TiO$_2$ particles were used to assess the influence of the chemical modification in the compatibility of polymer and particle, to disperse and distribute them in the polymer matrix. The sample codes are listed in **Table 1**. The composites and nanocomposites were prepared by the melt method in a single-screw extruder (AX Plásticos model AX 1626) with L/D ratio of 26 and screw diameter of 16 mm, containing three heating zones, coupled to a traditional bath and pelletizer. The processing parameters were temperatures of 160°C, 170°C and 190°C, referring to the feed, compression and homogenization zones, respectively, rotation of 40 rpm and pelletizing rate of 19%. The matrix used was the conventional type for production of pellets. The pure PP was prepared in the same way to provide a standard for comparison with the nanocomposites obtained [21].

2.2. Characterization

2.2.1. Differential Scanning Calorimetry (DSC)

The DSC curves of the samples were obtained under N$_2$, calibrated with an indium standard. The analysis

Table 1. T$_1$H values for TiO$_2$, TiO$_2$ modified with propionic acid and TiO$_2$ modified with propionic acid and octadecyl amine.

Samples	T$_1$H
TiO$_2$	14
TiO$_2$ modified with propionic acid	12
TiO$_2$ modified with octadecyl amine	11

involved a first heating from 10°C to 200°C followed by fast cooling (100°C/min), followed by another heating cycle of 20°C/min, from 20°C to 240°C.

2.2.2. X-Ray Diffraction (XRD)

X-ray analyses were done in a Rigaku D/Max 2400 diffractometer, with nickel-filtered CuKα radiation of wavelength 1.54 Å, at room temperature. The 2θ scanning range varied from 2° to 30°, with 0.05° steps, operating at 40 KV and 30 mA.

2.2.3. Nuclear Magnetic Resonance Spectroscopy (NMR)

The NMR acquirements were obtained using a Bruker 300AVANCE NMR spectrometer, operating at 75 MHz for carbons detection and 300 MHz for proton detection. Protonspectra were obtained by accumulating 8 K data points over a spectral width of 4400 Hz, using a 7.0 μs, 90 pulse with a recycle delay of 4 s between acquisitions. ^{13}C NMR, spectra were obtained with accumulation of 32 K data points covering a spectral width of 22 000 Hz, and a 5 μs, 90 pulse.

3. Results and Discussion

3.1. DSC

Based on DSC results, the melting temperatures (Tm) and the crystalline temperature (Tc) of the studied PP systems were determined to evaluate the possible changes in their values related to PP. The values of these thermal parameters for pure PP were 161°C and 121°C, respectively. Analyzing the materials prepared with PP and TiO$_2$ modified or not, the thermal parameters of the polymer matrix did not change, which is an indication that the particles did not influence processing stability and no degradation was detected.

2.2. XRD

Figure 1 exhibits the X-ray diffratograms of TiO$_2$, unmodified particle and particle modified with propionic acid and octadecyl amine.

The crystallinity degree of the materials containing unmodified TiO$_2$ did not change significantly, in a while for the materials prepared with organically modified TiO$_2$ changes, it increases for the samples containing 0.25% of organic modification and for the others proportions does not change significantly. We believe that the small proportion of organically modified TiO$_2$ could act as a nucleant particles, being nuclei for the matrix growth.
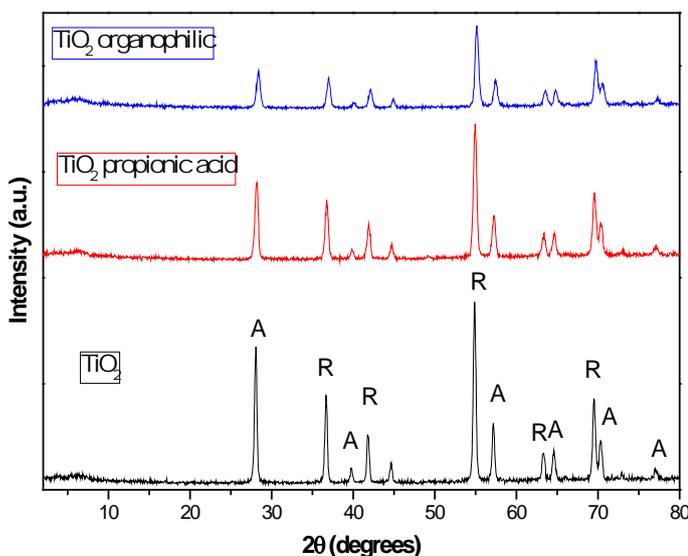
Figure 1. X-ray diffractogram of TiO$_2$, unmodified particle and particle modified with propionic acid and octadecyl amine.

2.3. NMR

Organically modified and unmodified TiO_2 nanoparticles were used to investigate the effect of organic modification on their dispersion and distribution in the PP matrix. The molecular dynamic behavior of the PP/TiO_2 composites gives information on the microstructure of the composites. The NMR results were analyzed in terms of the effect of the organic modification of the particles and the intermolecular interactions within the composites.

Table 1 listed the T_1H values for TiO_2, TiO_2 modified with propionic acid and TiO_2 modified with propionic acid and octadecyl amine (C-18).

The proton spin-lattice relaxation time values presented the same behavior than X-ray and thermal degradation temperature.

The behavior of $T_1\rho H$ for CH_2 and CH_3 group for all samples is shown in **Figure 2**, while that **Figure 3** and **Figure 4** shown the behavior of $T_1\rho H$ decay for CH_2 and CH_3 groups as function of B1 strength for sample PPm0.5% and for sample PPN1%, respectively.
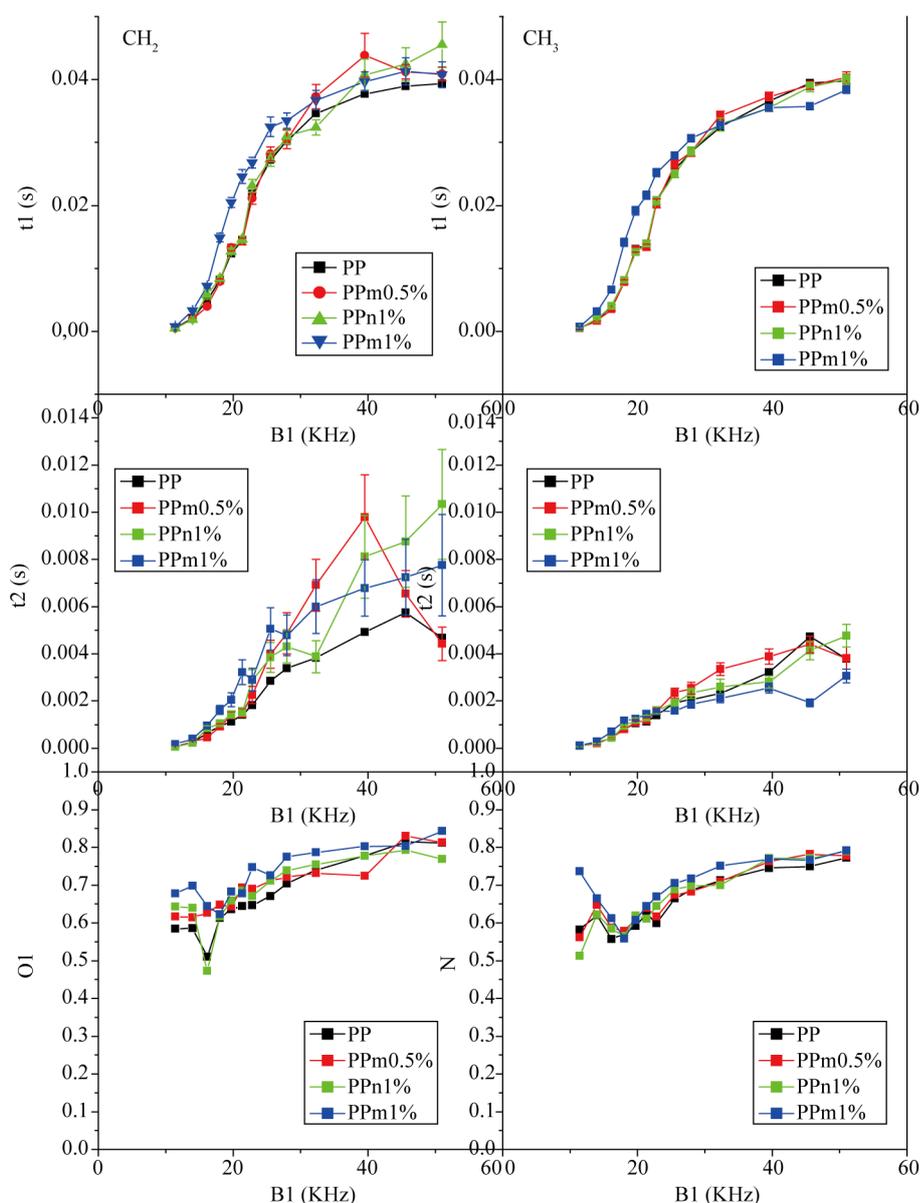
Figure 2. $T_1\rho H$ behavior for CH_2 and CH_3 group for all samples.
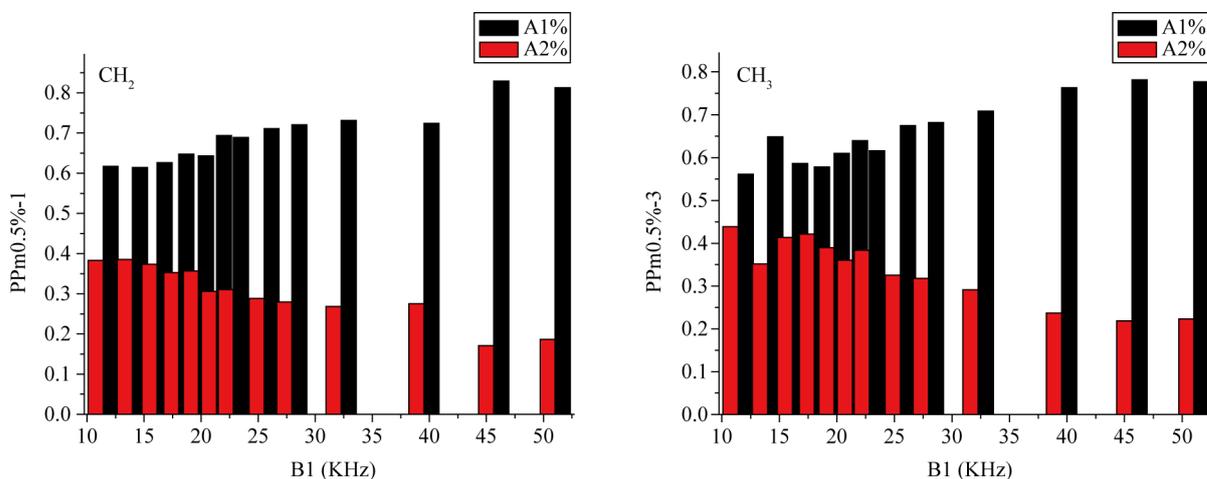
Figure 3. The behavior of $T_1\rho H$ decay for CH_2 and CH_3 groups as function of B1 strength for sample PPm0.5%.
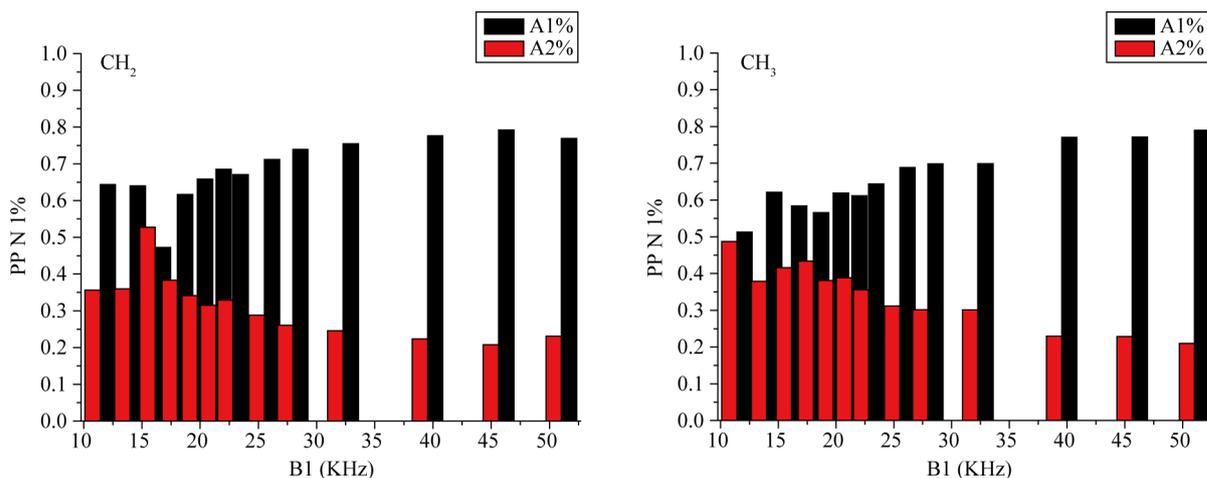
Figure 4. The behavior of $T_1\rho H$ decay for CH_2 and CH_3 groups as function of B1 strength for sample PPN1%.

According to the measured $T_1\rho H$ values, all composites showed at least two dynamic domains: the short values were related to the rigid part of the system, which includes the crystalline and the highly constrained amorphous phase, while the longer relaxation times were attributed to the less constrained amorphous region, which has higher molecular mobility compared to the rigid region of the materials.

For all systems, the dispersion and distribution of the particles in the polymer matrix was detected. The increase in the relaxation time parameter in the composites compared to the pure PP was associated to the strong interaction between titanium dioxide particles and the polymer chains. This effect was more pronounced for the systems containing organically modified.

The increase of relaxation times values in the composite materials compared to the pure PP was associated to the strong interaction between titanium dioxide nanoparticles and the polymer chains. This effect was more pronounced for the systems containing organically modified TiO_2.

Conclusions

TiO_2 particles were organically modified; these treatments promoted an improvement in the interaction and consequently the dispersion of this nanoparticle in the polymer system. Thus, the best PP/TiO_2 sample contained with 0.50% of modified particles.

According to all results, it could be inferred that intermolecular interactions occurred mainly with CH_2 and CH groups, being more intense with CH_2 groups.

Finally, the solid state high resolution NMR techniques were able to evaluate the proton resolved molecular dynamics of those systems.

Acknowledgements

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