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The Evaluation of Polyethylene/Clay Composite from Solid State NMR

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ABSTRACT

Polymeric nanocomposites based on polyethylene (PE) and Brazilian natural montmorillonite clay (MN) were obtained by melt processing, using a twin-screw extruder. The main objective of this work is focusing on the characterization of composites materials by solid-state nuclear magnetic resonance (NMR). The solid-state NMR measurements were used to observe both polymer matrix (through carbon-13 and hydrogen nuclei) and the clay (silicon-29 and aluminum-27). The polymer matrix analyses were carried out applying solid state techniques, such as: cross-polarization magic angle spinning (CPMAS), variable contact time (VCT) and by the proton spin-lattice relaxation time in the rotating frame parameter ($T_{1\rho}H$), detected from the resolved carbon-13 decay of the VCT experiment and through the determination of spin-lattice relaxation time, T_1H (using low field NMR). The clay was analyzed by ^{29}Si and ^{27}Al, employing MAS NMR technique. From those techniques we can have principally response on clay dispersion in the polyethylene matrix, as well as the interactions between both components in the nanostructured material. The T_1H response was an important result which showed, that the materials formed, presented different molecular domains (according to the domain size that varied from 25 to 50 nm, measured by relaxation), considering the clay dispersion mode in terms of intercalation and/or exfoliation in the polymer matrix.

Keywords: *NMR, Polymer, Polyethylene, Clay, Montmorillonite*

1. Introduction

Polymeric composites are class of materials that employ a mixing of polymer and fibers or inorganic compounds. According to the type, size and form of inorganic filler incorporated in the polymeric matrix, polymer composites possess particular properties, *i.e.*, polymeric nanocomposite. The polymeric nanocomposite morphologies are a consequence of the formed nanostructure, which influences directly the final properties of these materials that are depended on the dispersion mode of the inorganic nanoparticle in the matrix [1-6]. Thus, the knowledge of filler dispersion is the key to understand the material application and it is also an important point to be evaluated. Several conventional techniques are normally used to characterize the filler dispersion, such as: electronic microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal analyses (DSC and TG). More recently solid-state nuclear magnetic resonance has been employed, with success, to better understand the nanostructure formed in the polymeric nanocomposite [7-12]. The success comes to the fact that solid-state NMR spectroscopy allows obtaining information on chemical molecular structure; components interaction and filler homogeneity dispersion at molecular level [7-16].

Solid-state NMR has become an indispensable analytical tool for the study of crystalline and amorphous materials as silicates; zeolites; concretes and glasses, for instance [17]. Nuclear magnetic resonance spectroscopy is the most powerful method to obtain information about the local environment of the aluminum; ^{27}Al, NMR signals from 0 to 14 ppm are attributed to octahedral coordinated aluminum [17] and the peaks between 50 and 60 ppm correspond to tetrahedral coordinated ^{27}Al.

It is known that solid state ^{29}Si NMR has been successfully applied to the study of a wide range of crystalline and amorphous silicates or other related materials [11]. There are five types of SiO_4 tetrahedral units designated as Q region (Q_0, Q_1, Q_2, Q_3 and Q_4) that can be assigned in the ^{29}Si NMR spectrum. Typical chemical shift values can be associated to Q region characteristic, such as: $Q_0 = -72$ to -82 ppm; $Q_1 = -82$ to -89 ppm; $Q_2 = -92$ to -96 ppm; $Q_3 = -100$ to -104 ppm; and $Q_4 = -110$ ppm. Q_0 is designated as a single tetrahedron, Q_1 as end group, Q_2 a middle group, Q_3 a branching site, and Q_4 a cross-linking group [18,19].

The main objective of this work was to study PE/MN nanocomposites by solid state NMR through ^{13}C (analyzing the polymer matrix), ^{27}Al and ^{29}Si nuclei (evaluating the clay structure), focusing to understand the dispersion and/or interaction between clay and PE polymeric chains.

2. Experimental

2.1. Materials

The polyethylene sample used in this study was supplied by Polibrasil, Camaçari, Bahia, Brazil, with Melt Flow Index: MFI = 7.0 g/10 min, 190˚C/2.16 kg and melting temperature was 160˚C.

The commercial montmorillonite clay (MMT) was supplied by Bentonite União Nordeste, Paraíba, Brasil.

2.2. Sample Preparation

The composite of polythene/montmorillonite, prepared at different ratios (1%, 3%, 5%, 7% and 10%), were obtained by melting in HAAKE 9000 plastograph, coupled with chamber of mixture Rheomix 600, equipped with a conical counter-rotate twin screw extruder (TW), at shear rate of 60 rpm, for 10 minutes at 180˚C.

2.3. Solid State NMR Characterization

High-resolution solid-state ^{13}C NMR spectroscopy experiments were carried out at room temperature in rotor of 7 mm of Zirconium using a VARIAN, model UNIT-Plus, 9.4 Tesla, spectrometer operating at resonance frequencies of 100.47 MHz, 104.3 MHz and 79.49 MHz for ^{13}C, ^{27}Al and ^{29}Si, respectively. The ^{13}C CPMAS spectra were measured with a 6 μs 90˚ pulse, a 2 s pulse delay time, an acquisition time of 20 ms, and 512 scans. All NMR spectra were taken at 300 K using broad-band proton decoupling and a normal cross-polarization pulse sequence. A magic angle sample-spinning (MAS) rate 6 kHz was used to avoid absorption overlapping. The proton spin-lattice relaxation time in the rotating frame was determined indirectly through the decay of each resolved carbon nucleus using the range of contact time established from 200 to 8000 μs, hexamethyl benzene (HMB) was used as external standard, the methyl carbons were assigned as 17.3 ppm. The ^{29}Si CPMAS NMR spectra were recorded with 4 μs ^{1}H 90˚ pulses, 1 ms of contact time, spinning rate of 6 kHz, and 10 s of recycle delay. Kaolin was used as external standard. ^{27}Al MAS NMR experiments were recorded at MAS with 8 kHz spinning frequency, with 0.2 s of recycle delay and $AlCl_3(H_2O)_6$ was used as external standard.

3. Results and Discussion

From the resolved ^{13}C nucleus decay pattern from a series of ^{13}C CPMAS NMR spectra of PE and their hybrids with MN, we can obtain information on carbon intermolecular interactions and molecular mobility due to its environmental. The decay profile of PE NMR signal is typical for one semi-crystalline material. Therefore, for its composites the profile decay changed to similar behavior of amorphous material, which is attributed to MN incorporation in the polymer matrix due to the changes promoted in the molecular organization, which gives us the first indication of some interaction between both composite components. The changes in the molecular organization after clay incorporation in the PE matrix comes from the fact that the clay could act as a nucleante, which causes changes in the chains organization from the morphology created in the new materials, containing intercalated and some exfoliated clay, even in low concentration. From the variable contact time experiment $T_1\rho H$ values were determined for each resolved carbon, and in this case only a signal from PE, at 33 ppm, was detected. From this NMR signal we could extract information on polymer matrix organization and intermolecular interactions after clay incorporation, because this parameter is sensitive to local motions in a molecular range due to its observation in the tens of kilohertz, and then domains with 1 to 4 nm size are observed since that their molecular motions are identical. **Table 1** summarizes the $T_1\rho H$ values determined for PE and its composites.

From the relaxation values determined for the composites present a higher molecular rigidity comparing to PE due to the decrease of this parameter, compared to PE itself. From uniform values of this parameter, it can be evaluated that these materials have the nanoparticles homogeneously dispersed, and the molecular domains have a similar size, this relaxation parameter shows domains in the range of 4 nm. Because $T_1\rho H$ evaluates in the rotating frame *i.e.* it is measured in the tens of kilohertz and it also has contributions from both proton spin-spin relaxation time and spin-lattice relaxation time, which makes their values be interpreted in relation to the homogeneity in the lower scale comparing to the other two relaxation parameter. Another important point is related to the T_{CH} time of cross-polarization transfer, only 3% of nanoclay presented lower time to cross-polarize, which suggests that this clay proportion was better distributed in relation to the others, showing to be the best clay ratio for this system. According to the relaxation

Table 1. $T_1\rho H$ values and the T_{CH} (time for cross-polarization) determined for each resolved carbons through variable contact time, for PE and its PE/MN hybrids with MN.

Amostra	T_{CH}	δ (ppm)	$T_1\rho H$
PE	207	35	18
PE1%MN	206	33	12
PE3%MN	191	33	11
PE5%MN	201	35	11
PE7%MN	222	33	10
PE10%MN	198	33	10

parameter, good intermolecular interactions are formed in the nanocomposites components, since the relaxation parameter decreases the spatial proximity also decreases, making the chains closer.

The optimum ^{13}C CPMAS spectra of PE and its hybrid composites were recorded to observe changes in the chemical shift and signal forms. In all spectra just one NMR signal located at 33 ppm was detected. No significant change was found in the chemical shift; however, significant changes in the signal form are evident, which supports the modifications in the molecular organizations after clay incorporation in the polymer matrix. The ^{13}C CPMAS spectrum for 3% of clay incorporation presented the base line narrow than the other, which is another indication of the formation of a material with good nanoparticle distribution.

Figure 1 exhibits the ^{27}Al MAS NMR of the hybrid composites with MN. The ^{27}Al nucleus inform on clay structural changes, after being dispersed in the polymer matrix. In this Figure the ^{27}Al MAS hybrid spectrum with 5% of natural clay showed a different profile comparing to the others, showing strong changes in the clay structure due to the interaction between both hybrid components, which was promoted by a formation of nanomaterials with part exfoliated and part intercalated. Then, ^{27}Al nucleus can be probe to accompany the clay dispersion and the morphology formed in the nanomaterials. The same behavior was already observed, using this nucleus as a probe to evaluate nanocomposite formation for the polypropylene and organoclay system [6].

Figure 2 shows the ^{29}Si MAS NMR spectra of PE hybrids with MN. Analyzing the solid state ^{29}Si MAS NMR spectra for the natural clay and its hybrids with PE at different ratios, it was verified that the natural clay presented an intensity NMR signal located at –95 ppm (Q_2) and another one less intense in –110 ppm (Q_4) [18,19]. For the hybrids with 1 to 5% of clay only a broad signal centered at −95 ppm were detected, showing strong changes in the clay organization due to the polymer insertion among the clay lamellae, which would promote an exfoliated and/or intercalated nanomaterial. The nanostructured mixed material presents a disorder of clay structure, which is characteristic of nanomaterial formation. Therefore, for samples with higher ratio of clay (from 7% to 15%), they presented narrow signals as was found for lower clay ratio, suggesting a phase separation, and consequently no nanocomposite formation. This re-

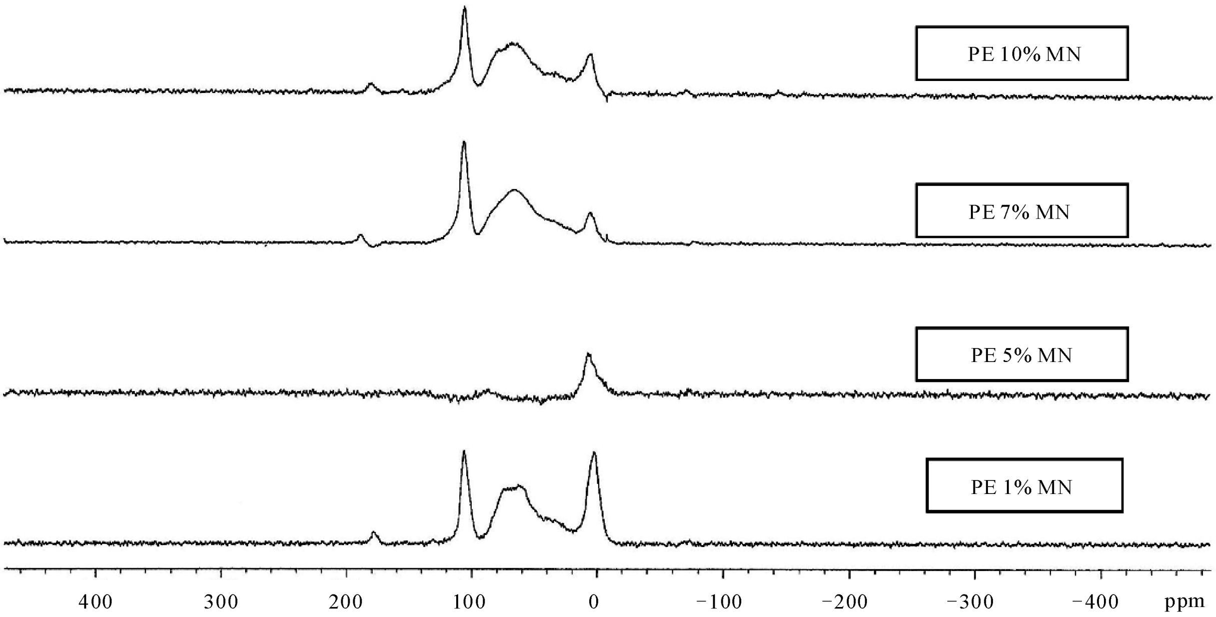

Figure 1. ^{27}**Al MAS NMR of hybrid composites with MN.**

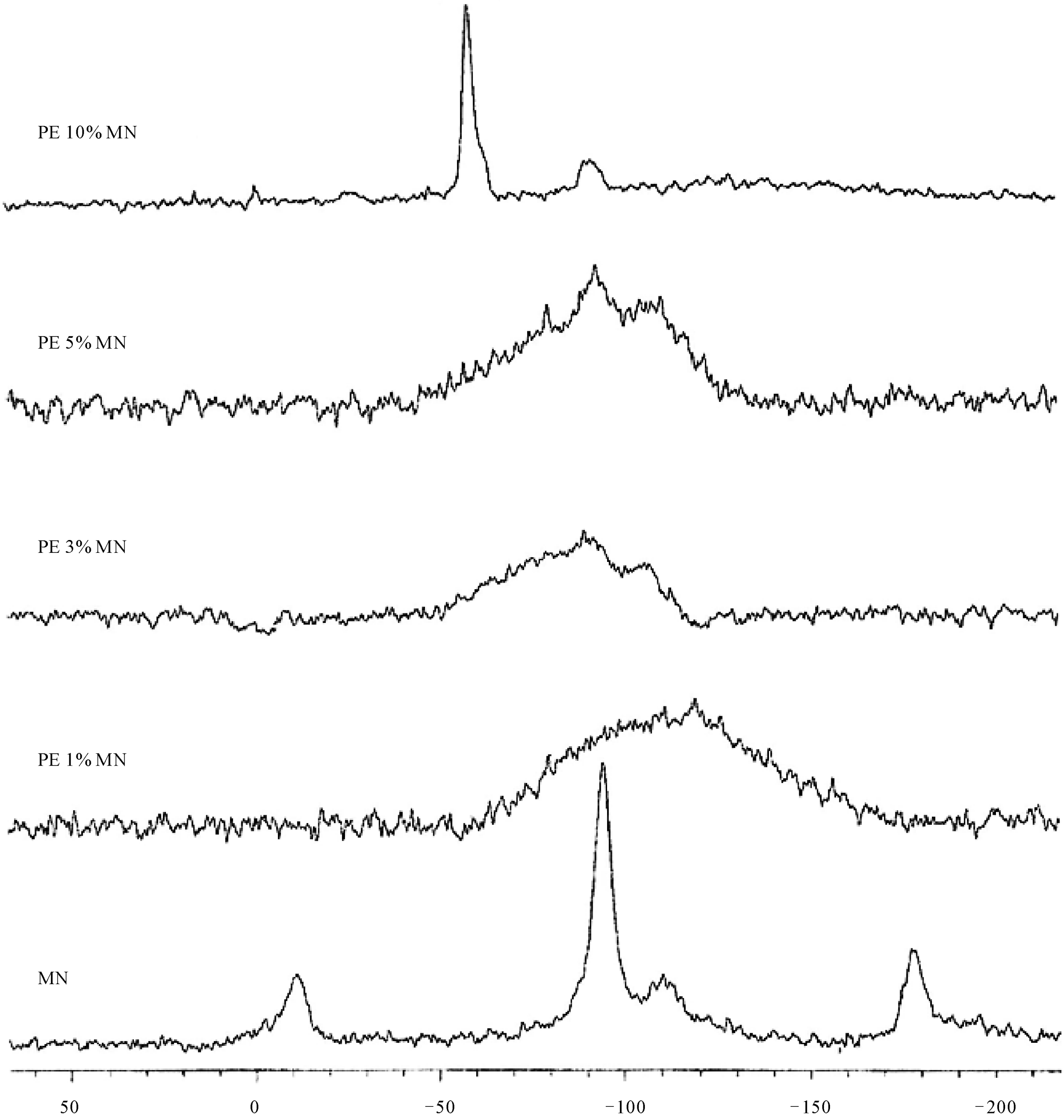

Figure 2. ^{29}**Si MAS NMR of MN and its hybrid composites with PE.**

sult indicates that high quantity of clay cannot be well dispersed in the polymeric matrix, as it was obtained for the low ratios, both situations behavior differently the first one has this behavior because high quantity of clay are to much to be well dispersed, while low quantity of clay make them to small to be dispersed due to the local interactions making the clay lamellae be together.

4. Conclusions

The work proves that the use of solid state NMR can be considered an important tool to evaluate the changes in both polymer and clay. It also permits to infer on nanomaterial homogeneity in terms of clay dispersion in the hybrid material.

This method permitted us to have a view from polymer matrix and from nanoparticule.

The employment of ^{27}Al and ^{29}Si nuclei, to have response from the clay, was good source of information. Therefore, ^{29}Si nucleus was more sensitive to changes in the clay organization and was effective to show changes in the clay particle, which proved to be a best source of information on nanoparticule.

According to the results we can conclude that the main purpose of this work was achieved.

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