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THE USE OF SOLID STATE NMR TO CHARACTERIZE HIGH DENSITY POLYETHYLENE/ORGANOCLAY NANOCOMPOSITES

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Abstract. Recently the development of new materials, in special polymeric nanocomposites, formed by polymer and layered silicates, have gained attention. In this work nanocomposites based on high-density polyethylene matrix (HDPE) and organically modified clay were prepared by melt processing and characterized by the determination of proton spin-lattice relaxation time through solid state nuclear magnetic resonance (NMR) spectroscopy. This work has a proposal to add one quantitative technique to help the researchers to better evaluate polymeric nanocomposite, because NMR is an important tool employed to study both molecular structure and dynamic molecular behavior. The nanocomposites were mixed in a twin-screw extruder, varying the shear rate parameter: 60 and 90 rpm at 463 K. Nanocomposites obtained were characterized through X-ray diffraction; thermal analysis; impact resistance and nuclear magnetic resonance. The T_1H results showed that the samples present different molecular domains according to the clay dispersion, forming an intercalated and/or exfoliated nanocomposites. The measurement of relaxation time, using low field NMR, is a useful method to evaluate changes in the molecular mobility of nanocomposite and can infer whether the sample is exfoliated and/or intercalated, since lamellar filler is used.

Keywords: nanocomposites, low field NMR, high-density polyethylene matrix, clay.

1. Introduction

Polyethylene is a commodity polymer that has a lot of uses, especially for food packing, which are normally discarded quickly, causing several environmental problems. Researches have been done to improve this polymer degradation process. Many studies were carried out to obtain blends with polysaccharides, like starch, for example [1, 2], therefore only little improvement was obtained with these materials. Recently the development of new materials, in special polymeric nanocomposites, formed by polymer and layered silicates, have gained attention [3-5]. The high density polyethylene, HDPE, lamellar silicate nanocomposite may improve the HDPE properties and may induce better environmental degradation, when they are discarded [6-9]. However, the complete knowledge of the nanomaterial behavior in relation to its structure/microstructure and intermolecular interactions, as well as nanoparticle dispersion will allow us to obtain responses to their final properties and consequently their uses.

According to this context, the determination of proton spin-lattice relaxation time through solid state nuclear magnetic resonance (NMR) spectroscopy was chosen, because it is an important tool employed to study both molecular structure and dynamic behavior [10, 11]. It can generate new support and responses on nanocomposites intermolecular interaction and structure organization. The employment of solid state techniques will help us to observe changes in the structural/microstructural and dynamical behavior, focusing the molecular motion of the polymer chains [12-14]. Generally speaking, polymeric nanocomposites are characterized by the conventional techniques such as: X-ray diffraction (XRD); transmission electronic micrograph (TEM); thermal analyses and mechanical properties [15-18]. Therefore, these techniques do not give a quantitative answer in relation to clay intercalation and exfoliation, for instance. It is well known that the increase of nanocomposites research needs a profound understanding of nanomaterials behavior. Thus, this work has a proposal to add one quantitative technique to help the researchers to better evaluate polymeric nanocomposite. Then, the use of some conventional techniques, such as X-ray, thermal measurements and impact resistance together with solid state NMR were applied as a methodology to obtain as many responses on nanocomposite, as possible, using low field NMR to give response on the molecular mobility of the polymer matrix, after organoclay is incorporated.

2. Experimental

2.1. Samples

The polyethylene sample used in this study was supplied by RioPol S/A, Rio de Janeiro, Brazil, and named as EI (Melt Flow Index: MFI = 7.0 g/min, 463 K/2.16 kg). The commercial montmorillonite organoclay (OMMT) was supplied by Bentec S/A. The nature of OMMT is bentonite clay, organically modified with a quaternary alkylammonium compound (C18). Both polymers and organoclay were used as received.

2.2. Nanocomposite Preparation

The blending was performed using melt processing in a torque rheometer, Rheocord 9000, Haake, equipped with a conical counter-rotate twin screw extruder (TWS), at a typical HDPE temperature processing (463 K), operating at 60 and 90 rpm. The nanomaterials obtained from the extruder were cut into pellets and analyzed directly in a low field NMR and in the thermal analyses. For X-ray characterization, the films were obtained by pressing the pellets. For the impact resistance, 8 measurements were done for each sample.

2.3. Materials Characterization

The extent of clay intercalation and/or exfoliation for HDPE/organoclay nanocomposites was observed by X-Ray diffraction (XRD) analyses. The films were characterized using an X-ray diffractometer, XRD 6000, Shimadzu, with nickel-filtered CuKα ($\lambda = 1.54$ E) radiation operated at 40 kV and 30 mA. The data were recorded at 2θ rates of $2°$ per minute. The basal spacing of nanocomposite was calculated using the Bragg's relation: $\lambda = 2d \cdot \sin\theta$.

The melting temperature and glass transition were determined for each sample using a DSC V4.4E (TA instruments) with the following conditions: nitrogen atmosphere 30 ml/min; heating velocity 10 K/min and temperature range 283–523 K. The TG analyses were carried out using a TGA 7 series (Perkin Elmer), with the range of temperature varied from 303 to 973 K, in nitrogen atmosphere, at a heating rate of 10 K.

The impact resistance measurements were carried out using Resil Impactor-Ceast (Impact Izod) instrument and the conditions used were in accordance with ASTM D 618; the samples were conditioned for 40 h at 296$\pm$ 2 K with 50 ± 5 % of relative humidity.

Low field NMR MARAN ultra 23 spectrometer, operating at 23 MHz (for protons), and equipped with an 18 mm variable temperature probe, was used for the determination of relaxation measurements. Proton spin-lattice relaxation times (T_1H) were determined directly by the traditional inversion recovery pulse sequence ($180°–$ $t–90°$). 90° pulse of 4.6µs was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty t data points, ranging from 0.1 to 5000 ms, with 4 scans for each point and 5s of recycle delay. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the program WINFIT. And the domain distribution was obtained by the WINDXP software. Both WINFIT and WINDXP were commercial programs and come with the spectrometer.

3. Results and Discussion

Processing parameters such as temperature; melt viscosity of polymer; mixing time and screw speed, must be evaluated to produce clay exfoliation. It is considered that high mixing speed may take a higher degree of clay intercalation and/or exfoliation. During nanocomposite preparation the clay dispersion was evaluated, and two mechanisms must be understood: the first one is related to the interlamelar clay spacing, which needs to be increased to facilitate polymer chains insertion; and the second one is the exfoliation process through the polymer chains intercalation.

The X-ray diffraction was employed to obtain information on nanocomposite crystalline ordination. The XRD results (Fig. 1) showed that polyethylene chains were intercalated into organoclay lamellae. A slight shift in the (d001) peak is observed at lower angles for all HDPE/ nanoclay compounds, related to a similar position. Table 1 shows the relationship of nanocomposites ratio, rotation processing and XRD data for OMMT, and EI/OMMT nanocomposites at the two shear rates evaluated. The presence of intercalated systems was identified from the basal spacing of organoclay, due to the increase of it with the incorporation of OMMT, as shown in Table 1. Analysing these data, when the EI/OMMT was processed at 90 rpm, the same behavior was not observed when the material was processed at 60 rpm. This behaviour could be explained by the diffusion of the polymer matrix. In this specific case the diffusion mechanism would be dominant comparing to the shear rate effect. Thus, from the XRD diffractogram, it was not observed an indication of an exfoliation process. It can be partially concluded that the ratio of intercalation/ exfoliation process, depends on the shear rate as well as the structural diffusion of HPDE.

The thermal analysis through differential scanning calorimetry and thermal analyses were carried out to evaluate changes in the glass transition temperature, melting temperature and thermal stability. The thermal evaluation of nanocomposites was done by DSC measurements and thermogravimetric analysis (TG). The obtained thermal data are listed in Table 2.

DSC data showed no significant difference for both HDPE/OMMT nanocomposites, comparing the thermal parameters *Tm* and ΔH with the polyethylene itself. These data show that the organoclay did not cause a significant change in the molecular mobility scale. From *Tm* no change in the crystallization process of nanocomposite matrix was
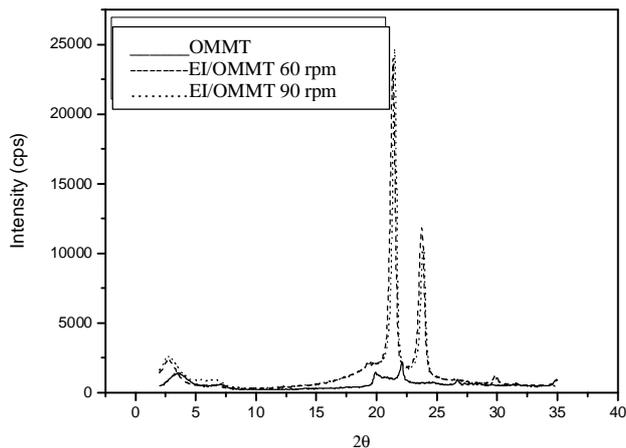
Fig 1. XRD patterns of OMMT (ss); EI/OMMT nanocomposites processed at 60 (———) and EI/OMMT nanocomposites processed at 90 rpm (…….)

Table 1

Relationship of nanocomposite ratio, shear rate and XRD data for OMMT and EI/OMMT nanocomposites at the two shear rates

Material type	Nanocomposite ratio (EI/OMMT)	Shear rate, rpm	XRD	
			2θ	d-spacing, Å
OMMT	0/100	-	3.2	27.6
EI/OMMT	95/5	60	2.8	31.5
		90	3.1	28.5

determined comparing to PE itself. However, a small decrease in the TG temperature for the both nanocomposites was detected because the polymer sample is less compacted by the presence of the clay, and so more susceptible to the heating of these materials, due to the incorporation of the polymer in the basal spacing. The thermal measurements data reveal that these techniques could not be sufficient to give response to the intercalation/ exfoliation process, because of its observation scale, which is about 100 nm. Thus, the nanocomposites were evaluated by the determination of the HDPE matrix and both nanocomposites impact resistance. The results showed a small decrease in the value of this parameter from 37 J/m (polyethylene) to 31 J/m (nanocomposites). This small decrease indicates that the sample would be partially exfoliated and partially intercalated, and may corroborate with the response obtained by TG analyses. The mechanical property results suggest the nanocomposite formation. According to the previous results, it is evident that the materials formed should be better evaluated, applying another technique that analyses the nanocomposite with more details. Thus, we have decided to employ proton NMR relaxation time, as this measurement is not destructive and the values of this parameter reached responses on sample organization, heterogeneity and particles dispersion. The relaxation data were important to understand the changes in the molecular

structural organization and molecular dynamic of the nanocomposite formed.

The hydrogen relaxation data for the samples, measured by low field NMR, are shown in Table 3. The T_1H results showed that the samples presented different molecular domains. Analyzing the polyethylene resin, before and after processing, two values for the relaxation parameter were found. One of them was attributed to mobile region (low value), which is constituted by amorphous phase and the other one was related to the rigid region (high value), formed by constricted amorphous and crystalline phase, which is normally responsible for the control of relaxation process. Considering the polyethylene/clay nanocomposite, (both are 5 % organoclay), processed at 60 rpm, four values were detected: a) the mobile region (low value – amorphous region); b) interface region, which is formed by polymer chains around the clay lamellae, that is the evidence of the exfoliation, because the metal present in the lamellae decreases the relaxation parameter c) and d) two crystalline regions. One of the crystalline phases is derived from the polymer crystallite near the clay lamellae, confirming the exfoliation processing. The higher value of relaxation data is from the polymer crystallite that is distant from the clay lamellae. The relaxation data support the first intercalation process suggested by X-ray and confirm an exfoliation process. Fig. 2 exhibits a diagram that suggests the nanostructure organization of the molecular domains formed in the HDPE/organoclay nanocomposites.

Table 2

DSC and TG results for EI and their nanocomposites with OMMT

Sample	*Tm*, K	ΔH, J/g	TG onset, K
EI	408	221	751
EI/OMMT 60	406	220	742
EI/OMMT 90	406	220	741
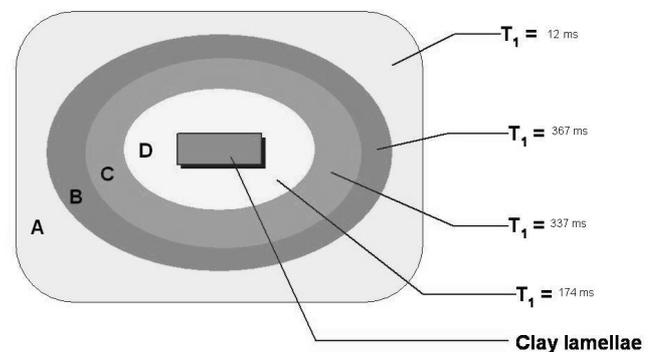
Fig. 2. Diagram of domain ordination in the formed nanocomposite

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Table 3

The low field NMR relaxation data of EI (resin and after processing) and EI/OMMT nanocomposite with 5 % of OMMT at 60 rpm

Sample	T_1H, ms	Domain intensity, %	Assignments
EI-resin	26	15	Mobile region
	334	85	Rigid region
Processed EI	18	18	Mobile region
	331	82	Rigid region
EI/OMMT 60 rpm	12 (a)	14	Mobile region
	174 (d)	30	Interface region
	337 (c)	27	Crystalline region (near to clay lamellae)
	367 (b)	29	Crystalline region (polymer matrix)

4. Conclusions

From the results obtained it can be concluded that the processing parameters affected the nanocomposites formation. The structural characteristics of polymer matrix were able to affect significantly the clay exfoliation process. The share rates were not relevant to the nanocomposite formation, for this system. The relaxation data showed different molecular domains for polyethylene and especially for nanocomposite. The measurement of relaxation time, using low field NMR, is a useful method to evaluate changes in the molecular mobility of nanocomposite and can infer whether the sample is exfoliated and/or intercalated, since lamellar filler is used.

Acknowledgements

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ВИКОРИСТАННЯ ЯМР ТВЕРДОГО ТІЛА ДЛЯ ХАРАКТЕРИСТИКИ ПОЛІЕТИЛЕН ВИСОКОЇ ГУСТИНИ /ГЛИНО-ОРГАНІЧНИХ НАНОКОМПОЗИТІВ

Анотація. Плавленням поліетилену високої густини як матриці та органічно модифікованої глини були приготовлені нанокомпозити та дано їх характеристику внаслідок визначення часу релаксації спін-граткового протону, використовуючи ЯМР-спектроскопію твердого тіла. В роботі запропоновано використовувати цю якісну характеристику для кращого оцінювання полімерного нанокомпозиту, оскільки ЯМР-спектроскопія є важливим методом вивчення одночасно молекулярної структури та динамічної молекулярної поведінки. Нанокомпозити готували перемішуванням при 463 К у двошнековому екструдері зі швидкістю 60 і 90 об/хв. Отримані нанокомпозити були охарактеризовані з використанням рентген-дифракції, термічного аналізу, міцності до удару і ядерного магнітного резонансу. T_1H результати показали, що зразки містять різні молекулярні домени диспергованої глини, утворюючи включені і/або розшаровані нанокомпозити. Вимірювання тривалості релаксації, використовуючи ЯМР слабкого поля (низької області), є придатним методом оцінювання змін в молекулярній мобільності нанокомпозиту і дає можливість визначити тип нанокомпозиту.

Ключові слова: нанокомпозити, ЯМР слабкого поля, поліетиленова матриця великої густини, глина.