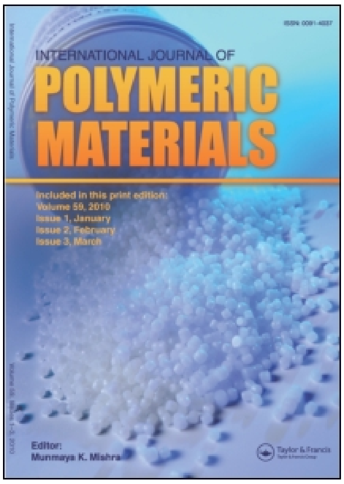

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Rodrigues, Tathiane C. , Tavares, Maria I. B. , Preto, Mônica , Soares, Igor Lopes and Moreira, Ana C. F.(2008) 'Evaluation of Polyethylene/Organoclay Nanocomposites by Low-field Nuclear Relaxation', International Journal of Polymeric Materials, 57: 12, 1119 — 1123

To link to this Article: DOI: 10.1080/00914030802428716

URL: http://dx.doi.org/10.1080/00914030802428716

International Journal of Polymeric Materials, 57:1119–1123, 2008

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030802428716

Evaluation of Polyethylene/Organoclay Nanocomposites by Low-field Nuclear Relaxation

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Two polyethylene (PE) samples (named BF and ES) were blended with 5% organoclay by melt processing at different shear rates. X-ray diffraction (XRD) showed that the organoclay was incorporated into the PE matrices. From the results it was determined that the level of intercalation was very similar for both systems. The knowledge of molecular dynamics of PE nanocomposites is very important since it depends on the clay dispersion. Thus, the objective of this work was to employ a new technique to understand changes in the molecular mobility for these systems. The samples were characterized by proton nuclear spin-lattice relaxation time (T_1H), which is measured in a low-field NMR spectrometer. The influence of the samples' preparation was evaluated through the relaxation data. For polyethylene resins, two values of relaxation parameter were found and they were attributed to mobile region (low value) and rigid region (high value). These values change after nanocomposite formation, confirming the changes in the resin matrix after organoclay was incorporated.

Keywords: clay, HDPE, nanocomposite, NMR

INTRODUCTION

High-density polyethylene, HDPE, is an important commodity polymer and it is very much used in food packaging and bags. The changes in the polyethylene molecular organization and mechanical properties after the introduction of nanoparticles, especially organically modified montmorillonite (OMMT) [1–5], makes this polymer

Received 31 May 2008; in final form 6 August 2008.
The authors would like to thank CNPq for supporting this work.

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more attractive industrially, since new products can have more higher values. To obtain nanocomposites with a higher percentage of exfoliated organoclay depends on the success of clay dispersion in the polymer matrix, which is related to the processing conditions [5–8]. It is well-known that the polymeric nanocomposites' properties are strongly dependent on the homogeneity of the nanomaterial. Thus, the knowledge of molecular structure and dynamic changes of these compounds became very important in order to obtain the response of the nanocomposite behavior [9–12]. In this context, the objective of this work was to prepare polymeric nanocomposites by melting intercalation of HDPE resins with a commercial organoclay at different shear rates, and to characterize the nanocomposites by X-ray diffraction (XRD) and through the measurement of proton spin-lattice relaxation times in the solid state, using low-field nuclear magnetic resonance (NMR). The relaxation data of solid-state NMR is a powerful technique to follow the dispersion and homogeneity of the solid sample.

MATERIALS AND METHODS

Materials

Two commercial grades of polyethylene were used: BF (copolymer of ethylene and 1-butene) and ES (high-density polyethylene), which were supplied by Rio Polímeros S/A Industry. The commercial organoclay is a montmorillonite modified with a quaternary alkylammonium (C-18) (OMMT), which was supplied by Bentec S/A.

Nanocomposite Preparation

The melt processing was performed by extrusion in a Haake Rhecord 9000 torque rheometer, equipped with a conical counter-rotate twin-screw extruder, at two shear rates: 60 and 90 rpm, at 190°C. After melt processing, the samples were cut into pellets and those were pressed at 190°C to obtain nanocomposite films. These were characterized by X-ray and proton spin-lattice relaxation time.

X-ray Diffraction

The X-ray diffraction (XRD) analyses were carried out using an X-ray diffractometer, XRD 6000, Shimadzu, with nickel-filtered CuKα ($\lambda = 1.54\,\text{Å}$) radiation, operated at 40 KV and 30 mA. The data were recorded at 2θ rates of 2° per min. The basal spacing of the nanocomposite was calculated using the Bragg's relation: $\lambda = 2d\sin\theta$.

Low-field NMR Characterization

All measurements of spin-lattice relaxation time, T_1H, were conducted using a low-field NMR spectrometer, Resonance Maran Ultra 23 (23 MHz for the hydrogen nucleus). The pulse sequence used was an inversion – recovery (recycle delay $180^\circ - \tau - 90^\circ$ acquisition). The 90° pulse, 4.6 μs, was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 5000 ms, with 4 scans each and 5 s of recycle delay. The temperature of the analyses was 27°C. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the commercial WINFIT program, which comes in the spectrometer.

RESULTS AND DISCUSSION

The XRD results of HDPE/OMMT nanocomposites obtained at two extrusion share rates (60 and 90 rpm) for both polymers demonstrated that the OMMT was incorporated into the polyethylene matrices, due to the slight shift of the (001) peak to lower angles region for both ES/organoclay and BF/organoclay.

These first results indicate that the chain structure characteristics of both polyethylene matrices could influence the organoclay dispersion. The polymer that presents a more mobile chain structure, BF, which is a copolymer of ethylene with low 1-butene content (about 4 mol%), indicated a better tendency to intercalation and/or exfoliation. For the ES homopolymer the results indicate a formation of intercalated system, preferentially. According to these results, a deeper study was employed. In this case we have chosen to measure the proton spin-lattice relaxation time, using a low-field NMR, to help better understand the changes in the molecular mobility of polymer matrix when the OMMT is incorporated into it and a nanocomposite is obtained.

Analyzing the ES polyethylene resin, two values of relaxation parameter were found. The low value was attributed to mobile region, due to a high degree of rotation, and the high value to rigid region, consisting of crystalline and constricted amorphous region. The latter generated by close contact to crystalline faces. The NMR relaxation data for ES/OMMT, obtained by both extrusion shear rates (60 and 90 rpm), also showed two values of T_1H parameter, confirming that these samples contained domains with different molecular mobilities. In both systems, free water from humidity absorption (lower relaxation values) was detected, due to the clay incorporation. Tables 1 and 2

TABLE 1 The Low-field NMR Relaxation Data of ES Resin and ES/Organoclay Nanocomposites

Sample	T_1H	Assignments
ES	29	Mobile Region
	311	Rigid Region
ESB60 rpm	6	Free water
	30	Mobile Region
	353	Rigid Region
ESB90 rpm	3	Free water
	39	Mobile Region
	362	Rigid Region

show the values of relaxation times measured for polyethylene resins and their nanocomposites.

Table 1 shows the T_1H relaxation data for ES resin, ESB60 and ESB90 nanocomposites. The values of T_1H parameter for both shear rate increases, comparing to pure resin, which is a strong indication that these nanocomposites are intercalated, as the polymer chains became less mobile, because they are constricted between clay lamellae.

Table 2 shows the relaxation values of T_1H for BF resin and BF/organoclay nanocomposites. For this polymer and its nanocomposites, the changes in T_1H values of the rigid fraction were found to be smaller than for the ES, which is an indication that the BF systems present a mixture of intercalated and exfoliated nanocomposites.

TABLE 2 The Low-field NMR Relaxation Data of BF Resin and BF/Organoclay Nanocomposites

Sample	T_1H	Assignments
BF	25	Mobile Region
	272	Rigid Region
BFB60 rpm	3	Free water
	29	Mobile Region
	283	Rigid Region
BFB90 rpm	4	Free water
	36	Mobile Region
	282	Rigid Region

CONCLUSIONS

Based on these results, it is apparent that the effect of the polyethylene structure is more important than the changes caused by the shear rates to promote the organoclay dispersion. We have seen here that both the NMR relaxation data and X-ray pattern showed that the polyethylene resins and their nanocomposites showed different behavior. The measurements of relaxation times using low-field NMR are an interesting method to study changes in the molecular mobility of nanocomposite formation, since the data obtained represents the median behavior of the hydrogens that belong to different domains. The combination of X-ray with relaxation data is a promising method to evaluate nanocomposites.

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