Ann. Magn. Reson. Vol. 3, Issues 1/2, 42-44, 2004 AUREMN ©

NMR Evaluation of Composites and Nanocomposites Obtained by Employing Polypropylene and Clay

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***Keywords*: NMR, polypropylene, nanocomposite, clay**

***Abstract**: Nanocomposites are interesting materials that present a peculiarity: they can show unexpected hybrid properties synergistically derived from two components.[1] To obtain a good nanocomposite, the clays layer should be exfoliated and dispersed. In this work we have chosen to prepare a nanocomposite using polypropylene, which is a commodity polymer with good properties, and Brazilian clay. Two types of hybrid nanocomposites were prepared in two different ways: one used a rheometer mix and the other used an extruder; the polypropylene/clay proportion was 95/5 w/w. The mixtures temperature was kept at 180 °C for 10 minutes. This work aimed to evaluate the characteristics of both types of obtained nanocomposites using solid state nuclear magnetic resonance (NMR). From ^{13}C CPMAS analyses no significant difference between the chemical shifts values of all ^{13}C derived from polypropylene in the nanocomposite was found, as compared to polypropylene. Therefore, not only changes in chemical shifts can be an indication of changes in morphology, especially when the polymeric matrix is formed. Indeed, changes in lineshape and intensity proportions also translate changes in sample morphology. Comparing the ^{13}C CPMAS NMR spectra of polypropylene with their nanocomposites prepared in the Haake and extruder we found that changes in the chains packing and ordination occurred, which pointed to the formation of a nanocomposite. To confirm these results, X-ray diffractograms were recorded. When the sample was prepared in the Haake only a composite was detected, but when the blend was performed in the extruder an exfoliated and dispensed nanocomposite was obtained.*

Nanocomposites are interesting materials that present a peculiarity: they can show unexpected hybrid properties synergistically derived from two components.[1-2] The nanocomposites promise new applications in many fields such as automotive and general/industrial applications, as well as from food (non-refrigerated packaging system capable of maintaining food freshness for three years) to medicine.[3-5] In this work we have chosen to prepare a nanocomposite blending polypropylene, a polymer with good properties with and a Brazilian clay (montmorillonite). This work aimed to evaluate the characteristics of both types of nanocomposites obtained, by using solid-state nuclear magnetic resonance (NMR). Polypropylene sample was supplied by Suzano Petroquímica. The organophylic clay was obtained using a sodium montmorillonite (MMT) clay, which was treated at room temperature with octadecylammonium salt.

Two types of hybrid nanocomposites were prepared by two different ways: using a rheometer mix or using an extruder. The polypropylene/clay proportion was 95/5 w/w.

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The mixtures were heated at 180 °C for 10, and the materials obtained were then kept at room temperature. To evaluate nanocomposites exfoliation and dispersion, the samples were analyzed by X-ray diffraction (XRD) and by solid state NMR. XRD analyses were carried out on a Rigaku miniflex diffractometer, operating at the Cu K α wavelength (1.542 °A). The ^{13}C solid spectra were obtained on an INOVA 300 spectrometer, operating at 75.4 MHz. All solid experiments were carried out at ambient probe temperature with high power decoupling. A zirconium oxide rotor of 7mm diameter was used to acquire NMR spectra at spinning rates of 5 kHz. ^{13}C NMR spectra were obtained using MAS, with a short recycle time (0.3 s) between 90° pulses and 5000 scans; in the CPMAS experiment, the strength of spin-locking field B_1 was 40 kHz; the recycle delay time was 2 s and two contact times were used (800μs and 1ms).

From ^{13}C CPMAS analyses no significant differences were found in chemical shifts values of all ^{13}C attributed to polypropylene in the nanocomposites, as compared to pure polypropylene. Therefore, not only changes in chemical shifts can be an indication of changes in morphology, especially when the polymeric matrix is formed. However, changes in lineshape and intensity proportions also indicate changes in sample morphology. Comparing the ^{13}C CPMAS NMR spectra of polypropylene with their nanocomposites prepared using the Haake and extruder, we found that changes in the chains packing and ordination occurred, which pointed to the formation of nanocomposites (Figure 1).

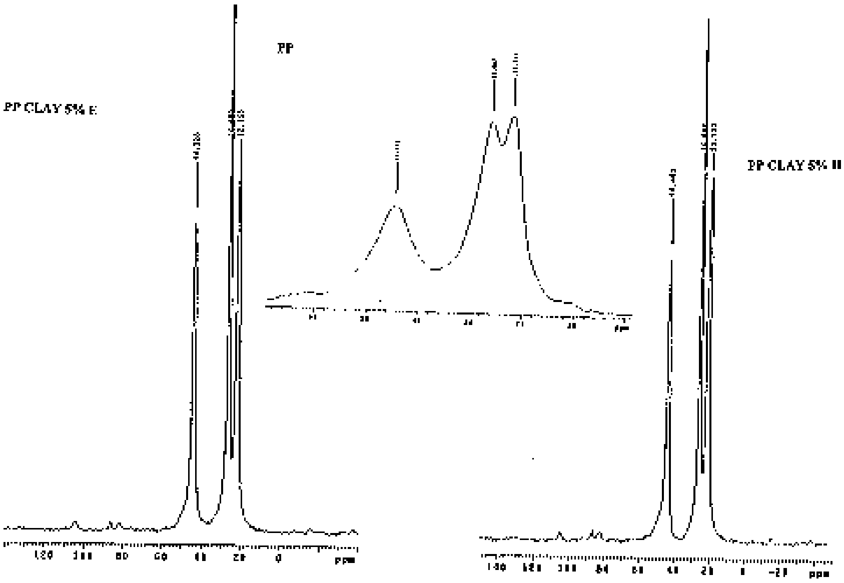

Figure 1. ^{13}C CPMAS NMR spectra of PP and their nanocomposite with clay

To confirm these results, characterization of the PP and PP/MMT samples were accomplished using the conventional nanoscale measurement of XRD (Figure 2). X-ray diffraction results indicate the increase in d(001)-spacing of Na^+-clay after introduction of quaternary ammonium salt. Disappearance of d(001) clay pattern was monitored during composite and nanocomposite preparation.

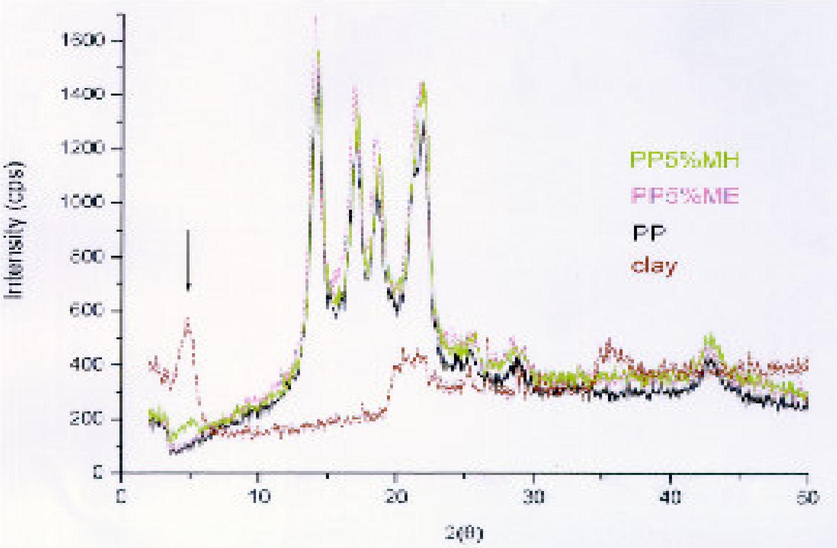

Figure 2. X-ray diffraction patterns of clay, organoclay, non exfoliated polypropylene-MMT and exfoliated polypropylene-MMT nanocomposite.

Both methods found that the sample extruded had an exfoliated morphology. This is evident from the XRD, because no peak of clay crystallinity was detected. For the sample prepared using Haake, only a composite was detected, but when the blend was prepared in the extruder, an exfoliated and dispensed nanocomposite was obtained.

Acknowledgements

The authors acknowledge CNPq for a scholarship.

References

1. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, *Macromolecules* **30** (1997) 6333.
2. J. M. Garces, D. J. Moll, J. Bicerano, R. Fibiger, G. David, *Advanced Materials* **12** (2000) 1835.
3. Y. Kurokawa, H. Yasuda, M. Kashiwagi, A. Oya, *J. Materials Sci. Letters* **16** (1997) 1670.
4. Y. Kurokawa, H. Yasuda, A. Oya, *J. Materials Sci. Letters* **15** (1996) 1481.
5. M. Okamoto, P.H. Nam, P. Maiti, T. Kotada, T. Nakayama, M. Takada, M. Ohshima, A. Usuki, N. Hasegawa, H. Okamoto, *Nano Letters* **1** (2001) 503.