



Skin effect of conductive polymer composites observed by high-resolution solid-state NMR



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ABSTRACT

High-resolution solid-state Nuclear Magnetic Resonance (NMR) combined with other investigations was applied to provide essential information on conductive polymer composites based on high-density polyethylene (HDPE) as matrix and multi-walled carbon nanotubes (MWCNTs) or silver nanoparticles (Ag-NPs) as fillers. All composites were prepared by melt mixing using an extrusion process and characterized electrically. By studying the general features of NMR spectra and the molecular dynamic from NMR relaxation parameters, it was possible to obtain structural information about the organization and dispersion of fillers. Due to the paramagnetic or conductive nature of the fillers, it was found that a loss of NMR signal occurred with increasing amounts of filler. In the case of Ag-NPs, this phenomenon was attributed to a skin effect caused by the conductive properties of fillers limiting the adsorption of radiofrequency.

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1. Introduction

Conductive polymer composites (CPCs) have been the object of intense researches recently [1–5]. The large potential applications and advantages of these composites mean they are privileged over many other materials [6–9]. Indeed, CPCs can serve in many sectors involving particular physical characteristics such as electric dissipation and shielding of electromagnetic interference (EMI) for use in automotive and aerospace domains.

Despite the large number of papers published in this area [10–14], there are still some important investigations which have not been published, as most studies have reported the electrical properties of these composites as basic results. A better description can be given when the later are interpreted in the scope of polymer microstructure and the organization/dispersion of conductive fillers. Some papers discuss the application of NMR as a characterization technique for interactions between filler and matrix in polymer composites [15–19], but there are very few reports concerning CPCs [20]. A reason for this limitation could be due to the conductive filler itself, as reported in a previous study of poly-

urethane/carbon-fiber composites where the paramagnetic residues of carbon fibers caused severe difficulties for NMR observations [20]. Also, there are no papers focusing on the characterization of CPCs when metallic fillers are involved. We believe that solid state NMR can also be applied in this case to complete investigations carried out with other techniques (electrical measurements, morphology, and microstructure...), giving information at the molecular level on the interactions between polymer chains and fillers when studying the chemical shifts and the relaxation parameters of the polymer matrix [21–23].

In this work, ¹³C NMR spectra were recorded using either direct excitation (HPDEC-MAS) or proton-to-carbon cross-polarization (CP-MAS) experiments under magic angle spinning on two types of CPCs (PE/MWCNT and PE/Ag-NPs). The effect of the incorporation of the conductive fillers on the chemical shift and line width was discussed. From the ¹³C magnetization build-up curves recorded under CP MAS condition as a function of the CP contact time, the proton spin lattice relaxation time in the rotating frame ($T_{1\rho H}$), and the cross-polarization transfer time (T_{CH}) were computed. These time constants are known to be related to the molecular dynamics of the polymer chains [24]. Moreover, the effect of the amounts of conductive fillers on those constants and on the whole observed NMR signal was also studied in detail.

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2. Experimental

2.1. Sample preparation and composition

Two series of polymer composites were investigated by solid-state NMR in this study. The first was high-density polyethylene (HDPE) filled with multi-walled carbon nanotubes (MWCNTs), which are conductive fillers with a high aspect ratio ($l/d \sim 160$), and the second series was HDPE filled with silver nanoparticles (Ag-NPs) with an average diameter of ~ 100 nm. All composites were produced in melt state by extrusion using a co-rotating twin-screw mini-extruder (Micro 15 Twin-Screw DSM research) to obtain conductive polymer composites. More details about the preparation and characterization can be found in [25,26].

Table 1 presents the composition of the samples studied by solid-state NMR. The filler loading is given as a volume fraction, which is more reliable for the explanation and interpretation of the data obtained from NMR and electrical conductivity characterizations.

2.2. Experimental RMN setup

High-resolution solid-state ^{13}C NMR spectra were mainly recorded on a Bruker Avance DSX 200 MHz spectrometer operating at 50.3 MHz for ^{13}C , using a combination of the proton-to-carbon cross-polarization, high-power proton decoupling, and magic angle spinning (CP/MAS) methods. The spinning rate was set at 5000 Hz. The ^1H radio-frequency field strength was set to give a proton pulse duration of around 3.103 μs ; the same value was used for the dipolar decoupling process. The ^{13}C radio frequency field strength was obtained by matching the Hartman–Hahn condition. Records of 1024 transients with contact time and recycle delay of 1 ms and 3 s, respectively, represented standard conditions. The chemical shift values were obtained via the glycine carbonyl signal, which was set at 176.03 ppm relative to tetramethylsilane (TMS). In order to obtain quantitative data, ^{13}C spectra were recorded with direct ^{13}C excitation with high-power proton decoupling during the NMR signal acquisition experiment. A 60 s recycling delay was used to assure complete relaxation of ^{13}C magnetizations.

In order to obtain $T_{1\rho\text{H}}$ and T_{CH} values, the carbon magnetization build-up under CP conditions was performed by varying the contact time values from 10 μs to 20 ms and worked out as described in the experimental section of one of our previously published articles [23]. From these experiments, $T_{1\rho\text{H}}$ and T_{CH} were computed by using the simplex fitting program (SIMFIT) provided by Bruker and Origin software. Dilution was performed by grinding the sample in a mortar with silica. Both compounds were precisely weighed, and the amount of material used to fill the 7 mm diameter rotors was also weighed. Therefore, the NMR signal areas were normalized taking into account the mass of polymer in each rotor and the number of transients acquired for each NMR experiment. Spectrum deconvolution was carried out with the DIMFIT program developed by Massiot et al. [27].

3. Results and discussion

3.1. General features of ^{13}C NMR spectra

The ^{13}C HPDEC-MAS spectrum of the pristine HDPE is shown in Fig. 1. A 60 s recycling delay was used, which allows quantitative data to be recorded. Deconvolution of the full signal leads to two distinct peaks (green and blue lines) at 32.4 and 30.6 ppm, assigned to the crystalline and amorphous phases respectively. Such attribution was confirmed by the CPMAS spectrum (not shown here), in which the carbon signal intensity of the crystalline

Table 1
Composition of studied composites.

Series	PE/MWCNT			PE/Ag-NP _s				
Filler loading (vol.%)	0	0.5	8.5	0	2	5	10	20

part was clearly enhanced. The crystalline domain contribution was found to be larger than the amorphous one. This is consistent with the results from X-ray and DSC experiments, which showed a high crystalline content in this PE.

Fig. 2a and b shows the HPDEC-MAS spectra of two polyethylene composites, HDPE/MWCNT loaded with 8.5 vol.% and PE/Ag-NPs loaded with 2 vol.%. As the whole NMR signal has been normalized for all samples to the amount of polymer inside the rotor, by comparing it with the spectrum of the pristine polyethylene (Fig. 1), significant decreases of the signal intensities were recorded for most of the filled PE (see Table 2). However, a third peak with very small intensity was also observed around 33 ppm in the case of PE/Ag-NP composites. This peak was almost undetectable in the unfilled PE because of its very low intensity. The origin of this peak could be related to the monoclinic phase of HDPE as reported previously [28].

3.2. Line widths, chemical shifts, and normalized areas

The values of signal chemical shifts and widths for all composites are listed in Table 2. On one hand, the chemical shifts of carbon signals for all lines were not altered by the incorporation of conductive fillers in both types of composites. This means that the chemical environments of the analyzed carbon atoms are not drastically modified and no strong interactions between polymer matrix and fillers can be depicted. On the other hand, addition of fillers leads to a broadening of the signals in both cases. Such findings have been reported for thermoplastic polyurethane matrix filled with carbon fibers and assigned to the difference in magnetic susceptibility between the fillers and polymer matrix [20]. Note that such interactions should be averaged by the spinning at the magic angle, which means that the broadening is probably due to hyperfine interactions. The broadening of signals when the MWCNT concentration increases compared to a merely stable widening in the case of PE/Ag-NPs indicates different behaviors

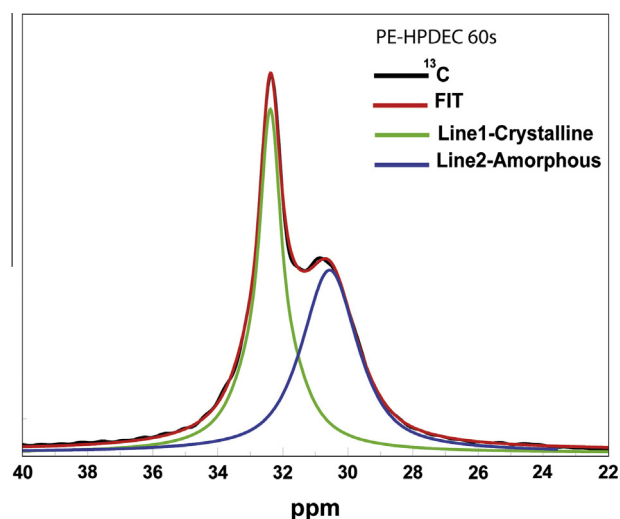


Fig. 1. HPDEC-MAS solid state NMR spectrum of the neat high-density polyethylene. Lines 1 and 2 represent the contributions of crystalline and amorphous phases respectively.

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