



# Dielectric relaxation of near-percolated carbon nanofiber polypropylene composites



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## ABSTRACT

In this work, the morphological, structural and dielectric analysis of near-percolated polypropylene (PP) composites containing carbon nanofibers (CNF) processing by melt-mixing are investigated. Whereas the morphological analysis shows that CNF exhibit some tendency to agglomerate within the PP matrix, the structural analysis showed first a general decrease in the intensity of the IR bands as a consequence of the interaction between carbon nanofibers and PP matrix and second an increase of the crystallinity degree of the PP/CNF composites when compared to the pure PP. The dielectric analysis demonstrates enhanced dielectric constants (from 2.97 for neat polymer to 9.7 for 1.9 vol% loaded composites at 200 Hz) and low dielectric losses. Furthermore, the dielectric relaxation for composites with concentrations in the vicinity of percolation is evidenced and well described by the generalized polydispersive Cole-Cole model from which the values of static dielectric constant ( $\epsilon_s$ ), high frequency dielectric constant ( $\epsilon_\infty$ ), distribution of relaxation time ( $\alpha$ ) and mean relaxation time ( $\tau_0$ ), are determined, suggesting that this latter analysis constitutes a strong tool for understanding the relationships between microstructure and dielectric properties in this type of polymer composites.

## 1. Introduction

Nanostructures composed of graphitic layers, including graphene and their derivatives, carbon nanotubes (CNT) and carbon nanofibers (CNF), are currently the focus of intense investigation [1]. In particular, CNF have a unique morphology in which exposed graphene edge planes are placed on the outer surface of the fiber [2]. Their outer and inner diameters ranging from 50 to 200 nm, and 30–90 nm, respectively, are slightly larger than CNT, while their lengths have average dimensions ranging from 50 to 100  $\mu\text{m}$  [3,4]. Furthermore, their excellent electrical ( $\sigma \sim 10^4$  S/m) and thermal ( $\tau \sim 1950$  W/mK) [5] conductivities along with their excellent mechanical properties, with an elastic modulus around 300 GPa and approximately 2.5 GPa in tensile strength [6], have converted CNF into an object of study in several fields of materials science [5,7,8]. For instance, an important area of application of CNF is the field of polymer composites. By incorporating different CNF loadings in a polymer matrix, important mechanical reinforcement [9], as well as, the enhancement of thermal, electrical and dielectric properties can be achieved [10,11]. In parti-

cular, it is known that CNF distributed in a polymer matrix can form into a large number of minicapacitors in a way that the final polymer composites can be used in applications which demands high electric permittivity such as electromagnetic radiation shielding [12], energy storage capacitors [13], actuators and sensors [14]. Accordingly, CNF/CNT have been used to fabricate polymer composites with improved dielectric constant due to their high electrical conductivity and aspect ratio [15–17]. On one hand, it is well known that for conducting polymer composites a percolation transition is established when connected networks formed by CNF/CNT fillers span the sample and several critical exponents associated with critical composition fluctuations have been determined [18]. On the other hand, it is commonly accepted that two relaxations processes are the main responsible factors for the enhancement of the dielectric properties in near-percolated materials: the interfacial polarization, associated with the charge trapping at the interface between the polymer and the filler and the space charge polarization at interfaces between the sample and the deposited electrodes [19]. However, the use of CNF/CNT fillers in dielectric polymer composites has been limited by several crucial

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challenges. The most important of them is that though dielectric constants can increase with the number of CNF/CNT present, mainly due to the two relaxation processes mentioned above, percolative composites have shown at the same time quite high dielectric losses due to the insulator–conductor transition near and beyond the percolation threshold [20]. To solve this problem, different strategies have been investigated. One approach is by preparing an insulating coating on the surface of carbon-based nanomaterials to avoid the composites become electrically conductive. For instance, Yang et al. prepared flexible dielectric polystyrene (PS) composites containing core-shell nanostructures consisting of polypyrrole (PPy) shell on core multiwall carbon nanotubes. By using this strategy, composites with dielectric constants up to 44 and low losses ( $< 0.07$ ) at 1 MHz for 10 wt % of CNT, were reported [21]. Other approach is to design composites with special structures, such as sandwich-like, layered and gradient structures. One example of this latter approach reports the processing of double-layer materials with one layer consisting of cyanate ester (CE) loaded with carbon nanotubes and other layer consisting of CE loaded with expanded graphite (EG) through two-step curing procedure [22]. A dielectric constant of 486 without dramatic high dielectric losses were reported for 0.5CNT/CE-5EG/CE systems with 0.5 wt% CNT and 5 wt% EG at 1 Hz. A disadvantage of both strategies is that they require the use of various materials, and additional physical and/or chemical processes which makes more costly and energy-consuming the final product. In this study, a simple strategy based on the effect that poor dispersion of low aspect ratio CNF in polypropylene (PP) has on the final dielectric properties, is proposed. The basic principle is that if percolation threshold is decreased with well-dispersed CNF, then the opposite (i. e. an increase of percolation threshold) must be true for worse dispersed systems, this latter effect would allow that larger amounts of CNF below percolation threshold can be incorporated in the matrix, and as consequence, an enhancement in the dielectric constant, without strong damage in dielectric losses of conducting nature, can be observed. Furthermore, though extensive research has been done regarding the effects of contents of different kind of carbon structures in the final dielectric constant and dielectric loss of polymer composites by using percolation theory [21,23], few reports have been focused on the analysis of their dielectric processes by phenomenological models which would enable to accurately determine the main characteristics of relaxation mechanisms over a broad frequency range [24]. For instance, Belattar et al. found that the Cole-Cole equation of dielectric relaxation, quantitatively described the experimental data in percolated carbon black (CB) filled ethylene butylacrylate (EBA) copolymer with nominal CB volume fractions between 0% and 22%, from which the relaxation time  $\tau_0$  (4.1 ms for 13 vol% of CB) and the parameter  $\alpha$ , associated with the distribution of relaxation time, with values from 0.06 to 0.10, were calculated [25]. The Cole-Cole formalism was used as well to calculate a relaxation time of 0.16  $\mu$ s in PE-CNT/CE double-layer materials consisting of 0.5 wt% filled CNT [26].

In summary, the principal aims of this work are: firstly, to demonstrate that near-percolated carbon based polymer composites processing by melt-mixing can be a very effective route to produce materials with enhanced dielectric constants and moderate low dielectric losses without damaging in mechanical enhanced properties, (associated with the increase of the elastic modulus and strength ascribed to the larger amount of CNF in the polymer, as it was discussed in our previous work [27]); and secondly, thanks to the quantitative determination of values of dielectric strength, relaxation time and distribution of relaxation time by using the Cole-Cole model, to contribute for the discussion of the origin of the relaxation mechanisms in the field of near-percolated carbon based polymer composites.

## 2. Materials and methods

### 2.1. Materials

A polypropylene (PP) powder, Borealis EE002AE, was used as

polymer matrix. One type of stacked-cup CNF used in this study (PR 25 PS XT), commercially known as Pyrograf III, were supplied by Applied Sciences, Inc. (ASI, Cedarville, OH, USA). PR 25 PS XT fibers have an average bulk density ranging from 0.0192 to 0.0480 g/cm<sup>3</sup> and an outer layer consisting on a disordered pyrolytically stripped layer. They have an average diameter of 120 nm and they have been heat-treated at temperatures of 1100 °C. They have shown to have lengths ranging from 50 to 100  $\mu$ m [28]. Compared to other grades PR 24 and PR 19 produced by this company, the PR 25 grade has lower iron content and a larger number of graphitic edge sites available along the length [29].

### 2.2. Fabrication of the CNF/PP composites

PP/CNF composites were fabricated, under the same processing conditions, on a modular lab-scale intermeshing mini-co-rotating twin-screw extruder, with a screw diameter of 13 mm, barrel length of 31 cm and an approximate L/D ratio of 26, coupled to a cylindrical rod dye of approximate 2.85 mm of diameter. A detailed description of the melt extrusion conditions has been previously published [27]. The extruded PP/CNF composites were then pelletized and pressed into compression-molded specimens with the appropriate square-form geometries for AC electrical measurements. At the end, composites with five CNF concentrations in polypropylene matrix from 0.5 to 2.4 vol% were prepared.

### 2.3. Methods

#### 2.3.1. Morphological characterization

Morphological characterization and CNF dispersion of the composites were examined using a JEOL JSM-6400 scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The samples were broken under cryogenic conditions and then sputter-coated with a thin layer of gold before testing.

An analytical TEM (JEOL JEM 1010) was used to observe the morphology of CNF. Fiber samples was dispersed in isopropanol and a drop was placed in a grid for direct observation.

#### 2.3.2. Structural characterization

Infrared measurements (FTIR) were performed at room temperature with IRAffinity-1S (Shimadzu) in ATR mode from 4000 to 380 cm<sup>-1</sup>. FTIR spectra were collected with 40 scans and a resolution of 4 cm<sup>-1</sup>, at room temperature. The crystalline structure of the composites was evaluated from XRD patterns recorded at room temperature using a Rigaku smartlab diffractometer with a copper ( $K\alpha_{1,2}$  radiation  $\lambda=1.540593$  and  $1.544414$  Å) anode x-ray tube operated at 9 kW (40 kV e 200 mA). Samples were scanned using a  $\theta/2\theta$  mode in a range from 2° to 10° (corresponding to a lattice spacing range between 44.14 and 8.84 Å) with a 0.04 deg step size. The degree of crystallinity of the polypropylene matrix was estimated using the following equation:  $CI (\%)=A_C/A_T$  where the  $A_C$  is the sum of the all areas of deconvoluted crystalline peaks, and  $A_T$  represents the total area of the XRD spectra. Deconvolution into subpeaks was performed by least-squares peak analysis software, XPSPEAK version 4.1, using the Gaussian/Lorentzian sum function and Shirley-type background subtraction. The components of the various spectra were mainly modeled as symmetrical Gaussian peaks for the best fit.

#### 2.3.3. AC Electrical characterization

Composites with CNF concentrations from 0.5 to 2.4 vol% and PP neat samples were compression molded into square films of dimensions 0.5×10×10 mm<sup>3</sup>. Au electrodes were deposited in both sides by thermal evaporation method. The capacity (C) and dissipation factor (tan  $\delta$ ) were measured at room temperature, in the 200 Hz to 20 MHz frequency range, with an AC applied signal of amplitude 0.5 V, using an automatic Quadtech 1929 Precision LCR meter. The real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex permittivity ( $\epsilon^*=\epsilon'-i\epsilon''$ ) were then

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