



Strong increase of the dielectric response of carbon nanotube/poly(vinylidene fluoride) composites induced by carbon nanotube type and pre-treatment

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ABSTRACT

The dielectric properties of multi walled carbon nanotube/poly(vinylidene fluoride) (CNT/PVDF) composites show large variations with carbon nanotube (CNT) type and fillers treatment during composite preparation. A preparation method involving toluene dispersion and corona discharge treatment has been developed allowing to obtain a maximum dielectric constant above 3000 and dielectric losses around 2.8 in a CNT/PVDF composite with 0.0419 CNT volume fraction. The electrical conductivity and dielectric response increase with CNT concentration within the composite with a strong variation around the percolation threshold. The main mechanism responsible for the large value of the dielectric constant is related to the preparation method, leading to an increase of the percolation threshold through the formation of a network of capacitors and resistors randomly connected in series and parallel. It is shown that the toluene and corona discharge methods decrease the electrical conductivity of the CNT/PVDF composite, increasing the dielectric response.

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1. Introduction

Carbon nanotubes (CNTs) have been increasingly used for applications due to their excellent electrical and mechanical properties [1–4]. The intrinsic properties of CNT depend on their aspect ratio (AR), chirality and the presence of impurities and defects [5]. Though typically used for improving electrical conductivity and mechanical properties of polymers, CNT/polymer composites have been recently developed with the objective of increasing the dielectric response of polymers, leading to larger dielectric constant values than the ones typically obtained for ceramic/polymer composites [6–8]. Further, as lower filler volume fractions are used, the composites also show improved mechanical properties. The increase of the dielectric constant is related to variations in the percolation threshold for the high aspect ratio fillers, giving rise to the so-called high-*k* dielectric materials [4,9,10]. The overall properties of composites with carbon nanoallotropes strongly depend on polymer type and composite preparation method, CNT dispersion and orientation as well as on CNT cluster size and distribution

[5]. As the dielectric constant (ϵ') of common polymers is typically smaller than 10 [11], these high dielectric constant composites enable their use as high-*k* materials in electronic devices [10].

In CNT/polymer composites there is a critical concentration, the percolation threshold, at which the electrical properties suffer strong variations [4,12]. The percolation threshold is affected by the aspect ratio and intrinsic characteristics of the CNT as well as by the composite processing method [4].

Beyond CNT or others carbon nanoallotropes, ceramic and metallic nanoparticles are also being used for the development of high dielectric constant composites [13,14]. Large dielectric constant materials have been obtained [15], allowing applications such as high-pressure sensors and energy harvesting devices [16], actuators and transducers [17], electroluminescent devices [18], hydrophones [10] and biomedical imaging [10,13], among others. Further, electronic devices working at high frequencies require high dielectric constant materials, which combine good dielectric and mechanical properties [19].

The dielectric properties of polymers are much lower than for ceramic or metals and several strategies have been implemented to increase them through the development of composite materials [18].

It has been shown that the dielectric response of ceramic/polymer composites depends on the ceramic concentration,

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preparation method and polymer matrix. The most used ceramic filler is BaTiO₃, and the highest values reported in the literature range between $\epsilon' \approx 40$ and 200, depending on the preparation conditions and filler content [13,16–20], which reaches typically up to 30% volume content. On the other hand, for large ceramic loadings, the ceramic/polymer composites become fragile, preventing their use in flexible devices [21–23].

Thus, different carbon nanoallotropes, including graphite and graphene, are being used within different polymer matrices, the dielectric constant showing a strong increase with increasing filler concentration, for lower fillers concentrations that in their ceramic or metallic counterparts. Dielectric constant values up to 240 for graphite/epoxy composites [24,25] and 5100 for graphene platelets/poly(vinylidene fluoride) composites [11] have been obtained.

The overall properties of polymer composites depend on filler type and content, polymer matrix and preparation method [26], the compatibility and interface between filler and matrix improving the performance of the composites.

Among different polymer matrices, composites with PVDF have been investigated due to the unique properties of this polymer such as strong piezo-, pyro- and ferroelectric properties, flexibility, thermal stability and chemical resistance [27,28]. The electroactive properties of PVDF strongly depend on its phase, microstructure and degree of crystallinity, which in turn depend on the processing conditions [28].

It has been an increasing interest in CNT/PVDF composites with high dielectric constant [29–31]. Different CNT functionalization have been used, which result in strong variations of the dielectric response of the composites. Thus, pristine CNT/PVDF composites show a maximum dielectric constant around 1600 for 6% CNT volume fraction (ϕ_{CNT}), whereas ester and carboxyl functionalized CNT show a maximum dielectric constant of 2400 and 3600 for 6.5 and 8 ϕ_{CNT} , respectively, with maximum dielectric losses around 10 [31]. The oxidation state of the CNT also influences the dielectric response of the CNT/PVDF composites, with a maximum dielectric constant from 80 to 630, depending on the CNT oxidation state [32]. These materials have been developed for electrical and electronic engineering devices such as high-energy-density capacitors and electromagnetic-wave absorption [7], among others.

The dielectric constant and the electrical conductivity of composites are typically understood by the percolation theory [12,33].

Near the percolation threshold there are specific scaling laws that govern the system:

$$\epsilon' \approx (\phi_c - \phi)^{-s} \quad \text{for } \phi < \phi_c \quad (1)$$

where ϵ' is the dielectric constant of the composite, ϕ the volume fraction and ϕ_c the percolation threshold. The electrical conductivity can be expressed by:

$$\sigma \approx (\phi - \phi_c)^t \quad \text{for } \phi > \phi_c \quad (2)$$

where σ is the electrical conductivity of the composite. The power law exponents, s and t , are the critical exponents and only depend on the dimensionality of the system. For a 3D system s is between 0.7 and 1.0 and t is between 1.6 and 2.0 [33].

The percolation theory also predicts that near the percolation threshold:

$$\sigma \approx \omega^u \quad (3)$$

$$\epsilon' \approx \omega^{u-1} \quad (4)$$

where ω is the angular frequency and u is the critical exponent, which for a random resistor networks is ≈ 0.73 [34].

The formation of a conductive network where the conduction between the high aspect ratio fillers mainly occurs by hopping has been described [35] by:

$$\log(\sigma) \approx \phi^{-1/3} \quad (5)$$

It is important to notice that above the percolation threshold, the AC composite conductivity and dielectric constant can exhibit an anomalous power law dispersions.

Due to the fact that these power laws occur in a wide class of materials they were termed universal dielectric response [36,37]. The origin of these anomalous power law dispersions, i.e. the universal dielectric response, is the formation of a RC network where the resistors and capacitors are randomly connected in series and parallel. One of the characteristics of the universal dielectric response is the existence of a plateau for the dielectric constant at low frequencies that changes to a power law for higher frequencies.

In this context, this work reports on the production of high dielectric constant CNT/PVDF composites. The effect of CNT aspect ratio and preparation conditions, involving solvent dispersion and corona discharge are discussed. Thus, a simple and scalable method for the production of high- k materials is provided.

2. Experimental

2.1. Sample preparation

The preparation of the composites involved several steps, and in order to understand the influence of each different preparation step in the electrical response of the composites, a systematic variation of these procedures was carried out. The complete processing of the samples includes, initially, that a specific amount of CNT is placed in an Erlenmeyer, soaked in toluene and placed in an ultrasound bath for 6 h to promote a CNT disaggregation. Thereafter, toluene is evaporated in an oven at a temperature of 120 °C for 12 h. Then, the CNTs are subjected to an electric discharge of corona of 25 kV for 30 min to obtain rougher and shortened carbon nanotubes [36]. Finally, the CNTs are placed in dimethylformamide, DMF (Merck, 99% purity) and in an ultrasound bath for 6 h, to promote dispersion. In order to compare and discuss the effect of the processing conditions on the electrical and dielectric properties of CNT/PVDF composites, solvent dispersion with toluene and corona treatment have not been applied to all composites. Finally, PVDF was introduced in the Erlenmeyer and the solution was placed in a magnetic stirrer at room temperature for 2 h for complete dissolution of PVDF (1010, Solef) with a density of 1.78 g/cm³, melt flow index (MFI) of 6 g/10 min (5 kg at 230 °C), viscosity of 6000 Pa s and volume electrical resistance larger than 10¹⁴ Ω/cm.

Films were obtained by bar coating of the solution deposited on a glass plate. The films were then placed in an oven at a temperature of 120 °C for 30 min for solvent evaporation and cooled to room temperature. Finally, samples were melted at 230 °C for 15 min and cooled down to room temperature. In this way, the obtained polymer phase was the nonpolar α -phase of PVDF [28] and the samples were obtained with a thickness of 200–500 μm . The composite films were characterized for eight different CNT contents varying between 0.0000875 and 0.0419 ϕ_{CNT} corresponding to weight percentage (wt%) between 0.01 and 5%. To compare the influence of CNT type in the composites, three different carbon nanotubes were used, including double-walled CNT (DWCNT) and multi-walled CNT (MWCNT), from Baytubes and NanoAmor. The main properties of the CNT are shown in Table 1.

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