Dielectric behavior and electrical conductivity of PVDF filled with functionalized single-walled carbon nanotubes

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ABSTRACT

Polyvinylidene fluoride (PVDF)/ single-walled carbon nanotube (SWCNT) composites are characterized by X-ray diffraction and scanning calorimetry, and studied by dielectric relaxation spectroscopy (DRS) in the temperature range of -75 to 150°C. The effects of SWCNTs and SWCNT functionalization are analyzed in terms of α and α_c relaxation, dielectric permittivity, loss tangent, and AC electrical conductivity. Some small changes are detected in α relaxation with the addition of SWCNTs, and a strong influence of SWCNTs is observed in the other relaxation α_c . Below the percolation threshold, the dielectric permittivity of functionalized SWCNT composites increases compared to blank PVDF, without notable changes in the dielectric loss. All the composite systems show an electrical percolation behavior with different thresholds depending on SWCNT functionalization. Threshold concentrations remain nearly unchanged in the whole temperature and frequency ranges. The base PVDF conductivity strongly depends on temperature and frequency, while the maximum conductivity above the percolation remains nearly unchanged ($\sim 10^{-2}$ S/m) for all the systems, temperatures and frequencies.

KEYWORDS: Polyvinylidene fluoride, carbon nanotube, polymer relaxations, permittivity, alternating current, temperature

INTRODUCTION

Polyvinylidene difluoride (PVDF) is a thermoplastic polymer with a semicrystalline microstructure and a varied polymorphism, showing high compliance, thermal and chemical stability, and piezoelectric and pyroelectric properties. These properties are the base of different applications such as tactile sensors, infrared imaging devices, actuators, electrolyte-gated transistors, etc. [1, 2]. The incorporation of different nanofillers is a way to further improve the performance of raw PVDF and extend its applications. Probably, carbon nanotubes (CNTs) are among the most studied reinforcements due to their intrinsic characteristics including high aspect ratio, outstanding electrical and mechanical properties, and versatility for surface functionalization. The CNT/PVDF composites enable new applications in different sectors, including membranes for ultrafiltration [3], superhydrophobic surfaces [4] fuel cell electrodes, charge transport layers in sensor systems [5], high energy storage systems [6, 7], infrared detectors [8], electromagnetic interference shielding and radar absorbing coatings for military energy systems [9], electrodes for electrocardiograms [10], actuators and pressure sensors [11, 12], in-vitro muscle cell growth [13], and structural health monitoring systems [14]. A comprehensive description of the applications of CNT-based PVDF composites can be found in several reviews [15, 16].

The incorporation of small amounts of CNTs in an insulating polymer leads to an increase in the electrical conductivity by several orders of magnitude due to the percolation effect. The conducting network formation strongly depends on the one-dimensional character of CNTs and their suitable dispersion in the polymer matrix. The increase in conductivity is also associated to a strong variation in the dielectric constant, which is due to the insulating-conductor transition around the CNT percolation threshold. Such an increase in the dielectric constant is positive in some applications, for instance

energy storage in capacitors. However, it is usually accompanied by a strong increase in the loss tangent that reduces the composite potential applications. Therefore, it is necessary to find a way for increasing the PVDF dielectric constant, while maintaining the composite dielectric losses down at a suitable level. Different strategies have been developed in order to resolve this paradigm, including the incorporation of a secondary BaTiO₃ insulating filler [17], the surface oxidation of metallic nanowires [18], and others that have been widely summarized by Arjmand et al. [19]. One of the routes is based on surface modification of CNTs with different functionalization types including surface oxidation [20], nitrogen doping [21], and the incorporation of organic compounds such as polypyrrole [6]. These functionalizations have been mostly performed on multi-walled carbon nanotubes (MWCNTs), although single-walled carbon nanotubes (SWCNTs) have a higher aspect ratio and thus they are expected to make possible lower percolation thresholds and a larger density of nanocapacitors than MWCNTs. Similarly to MWCNTs, surface chemical modification of SWCNTs may be a way towards PVDF composites with high dielectric permittivity and low loss. So far, SWCNTs have been chemically functionalized with the aim of increasing the PVDF electrical conductivity and decrease the percolation threshold [22-25]. However, new studies are still needed to understand the effects of chemical functionalization on the macroscopic dielectric and electrical properties.

In this work we analyze the dielectric and conductive behavior of SWCNT/PVDF composites, where SWCNTs are untreated, functionalized by nitric acid treatment or functionalized with fluoroalkyl moieties. Previously, we have reported the mechanical elastic properties of the materials [24]. Here, the effect of nanofiller chemical modifications on PVDF dielectric relaxation and alternating current (AC) conductivity is studied in the temperature range of -75 to 150°C. Plots of the electrical conductivity vs.

SWCNT filler concentration are presented as a function of both temperature and frequency, allowing a study of the percolation threshold in the whole measured temperature and frequency ranges.

MATERIALS AND METHODS

For the current study, SWCNTs (AP-SWNT grade) were purchased from Carbon Solutions Inc., Riverside, CA, United States. This SWCNT powder material is synthesized by the electric-arc reactor method using Ni/Y catalysts and contains < 30 wt.% metal residue. PVDF powder ($M_w \sim 534,000$, ref. 182702) was purchased from Sigma-Aldrich, Madrid, Spain.

Pristine SWCNT powders were utilized as-received or functionalized by two different chemical procedures: nitric acid treatment (SWCNT-NIT) and functionalization with perfluorooctyl moieties (SWCNT-PFO). The functionalization procedures and the SWCNT/PVDF composite preparation have been previously described [24]. The SWCNT-NIT material was prepared by treatment with 1.5M HNO_3 in a reflux for 2 h. Oxygen functional groups are created during the nitric acid treatment, and most of the metal catalyst residues are eliminated. The PFO-SWCNT material was synthesized through the covalent bonding of heptadecafluorooctyl phenyl groups ($\text{F}_3\text{C}-(\text{CF}_2)_7-\text{C}_6\text{H}_4-$) to pristine SWCNTs, following the diazonium salts route. A complete characterization of the SWCNT functionalization is included in the Supplementary Data.

The preparation of SWCNT/PVDF composites consisted of a premixing stage in acetone followed by hot pressing inside a stainless steel round mold ($\varnothing = 13$ cm). A total mass of 11 g of SWCNTs + PVDF was suspended in ~ 100 mL of acetone with the help of an ultrasound bath. The mixture was kept in the ultrasound bath and at once stirred with a blade mixer until acetone was evaporated. Then the material was dried in an oven to

remove the trapped solvent. Finally, it was hot-pressed at 200°C under 2 Tm for 2h in a Specac laboratory press and left to cool down naturally inside the mold without any further pressure. Hereafter, the composites will be referred to as SWCNT-X/PVDF, SWCNT-NIT-X/PVDF, and SWCNT-PFO-X/PVDF for the non-functionalized, acid-treated and fluoroalkyl-functionalized SWCNTs, respectively, where X stands for the filler weight percentage, according to **Table 1**.

Structural characterization and dielectric measurements

X-ray diffraction (XRD) was performed in a Bruker AXS D8 Advance diffractometer using CuK α radiation. The polymer crystallinity (X_{XRD}) was calculated from data in the range of $2\theta = 12\text{-}24^\circ$. Differential scanning calorimetry (DSC) experiments were performed in a Mettler TA4000 calorimeter. The polymer crystallinity (X_{DSC}) was calculated as: $X_{\text{DSC}} = \Delta_m H / \Delta_m H_{100}$, where $\Delta_m H_{100}$ represents the melting enthalpy of a 100% crystalline sample of pure PVDF, which is 104.6 J g $^{-1}$ [26]. Some additional details of the XRD and DSC analysis are given in the Supplementary Data.

Dielectric measurements were performed using a dielectric spectrometry setup (Novocontrol BDS4000), which includes a two-terminal dielectric cell, a frequency response analyzer (Solartron 1250), and a high impedance preamplifier of variable gain. The complex dielectric constant was obtained by sweeping in the frequency range of 0.1 Hz to 10 5 Hz at different stabilized temperatures by heating from -75 °C to 150 °C in temperature steps of 5 °C. The samples were disks of a 12 mm of thickness, which were held between the condenser plates. The dielectric analysis was conducted through the complex dielectric permeability $\epsilon^* = \epsilon' - \epsilon''$, taking into account the dielectric constant ϵ' and the dielectric loss ϵ'' , as well as the $\tan\delta = \epsilon'' / \epsilon'$. The dielectric relaxations were analyzed in the isotherm spectra by fitting the response in the frequency domain to Havriliak-Negami (HN) curves (*Eq. 1*) [27, 28]

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{\{1 + (i\omega\tau_{HN})^\alpha\}^\beta} \quad (Eq.1)$$

where $\omega = 2\pi f$ is the frequency in radians/second, α and β are shape parameters respectively corresponding to the width and asymmetry of the relaxation time distributions, τ_{HN} is the Havriliak-Negami relaxation time, and $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the relaxation strength (ε_s and ε_∞ are the real part of the permittivity when $\omega \rightarrow 0$ and $\omega \rightarrow \infty$, respectively).

At sufficiently high temperatures, ohmic conduction due to charge carriers σ^* frequently dominates the loss contribution at low frequencies, potentially masking dielectric relaxations. In order to discriminate dielectric and conductivity effects, the conduction-free dielectric loss ε''_{NC} was also determined by Eq. 2 [29]

$$\varepsilon''_{NC} = \varepsilon'' - \frac{\sigma_0}{\varepsilon_0 2\pi f^s} \quad (Eq.2)$$

with f being the frequency in Hertz, σ_0 a pre-exponential coefficient, and s an exponent normally close to 1.

RESULTS AND DISCUSSION

Structure and microstructure

Five crystalline forms of PVDF have been identified, the most common ones being the α and β phases. The α -PVDF is easily produced from the polymer melt, while the β -PVDF, which is piezoelectric and pyroelectric, can be synthesized by crystallization from a solution or by drawing α -PVDF. **Figure 1** shows XRD and DSC results for neat PVDF and three SWCNT/PVDF composites with filler contents above the electrical percolation threshold. XRD analysis indicates that crystalline polymer domains are α -phase in all the cases. A decrease in the polymer crystallinity is calculated with increasing SWCNT

contents (**Table 2**). This fact is in part associated to a certain decrease in the (020) band intensity, which is most clearly observed for the SWCNT-NIT-7/PVDF material.

The presence of SWCNTs causes an increase in the PVDF crystallization temperature, and a decrease in the crystallization enthalpy (**Table 2**). The increase in the PVDF crystallization temperature upon the filler addition indicates that SWCNTs act as nucleation agents during crystallization. On the contrary, melting temperature does not substantially change upon the addition of SWCNTs. Melting enthalpy decreases with increasing SWCNT contents, indicating a decrease in the PVDF crystallinity, in agreement with XRD results. The melting temperature T_m is commonly applied to estimate the lamellar thickness L_c through the Gibbs-Thomson equation:

$$T_m = T_{m,0} \left(1 - \frac{2\sigma}{L_c \rho_c \Delta H_m^0} \right) \text{ (Eq. 3)}$$

where T_m is the polymer melting temperature, $T_{m,0}$ the equilibrium melting temperature of a perfect crystalline polymer, σ the specific surface energy, ρ_c the density of the crystalline phase, and ΔH_m^0 the melting enthalpy of a perfect crystalline polymer. Since melting temperatures are nearly identical for PVDF and all the composites, it is deduced that the thickness of PVDF crystalline lamellae does not substantially change. Therefore the decrease in the crystallinity degree might be associated to a reduction in the lateral size of crystalline lamellae. The presence of nanotubes initially favors polymer chain associations, while it decreases the long range order inside the lamellae. These microstructural effects, associated to the thermal response, have been previously observed in PVDF composites with double-walled CNTs [30], non-functionalized MWCNTs [31], other carbon-based nanoadditives [25], and even in functionalized MWCNT/PVDF-PMMA blends [32].

Another outcome of the X-ray diffractograms is that SWCNTs did not induce the formation of β -phase PVDF in our composites. This fact was also confirmed by infrared

spectroscopy (Supplementary Data). The observed behavior is different from that in some recent studies, as the presence of the reinforcement introduced dramatic changes in the β -phase percentage [33-36]. Moreover, Sharma et al. [36] reported that β -phase formation leads to the disappearance of certain dielectric relaxations. In our case, SWCNTs contribute to an increase in the α_c relaxation strength, as we will further comment in the next section, indirectly confirming that β -phase PVDF is not formed.

Dielectric relaxations

Figure 2 illustrates 3D temperature/frequency representations of the ϵ' and ϵ'' response corresponding to neat PVDF. Analogous maps were carried out for all the studied composites. For the unfilled material, both maps clearly show the presence of two relaxations at low/intermediate temperatures and a strong conductivity contribution in the highest temperature range. The relaxations will be labelled as α and α_c following most of the dielectric and mechanical measurements that can be found in the literature concerning the non-polar α -PVDF phase. The α relaxation is associated to the dynamic glass transition T_g , and thus it is related to cooperative segment motions within the main chain of the amorphous polymer region. The α_c relaxation is related to different imperfections of the α -phase crystallites, such as chain loops at the lamellae surface, discontinuities, etc. At temperatures below -70 °C, the material also presents the β relaxation, which is a secondary transition related to local movements of polar groups in polymeric chains. Our measurements did not allow the observation of β relaxation, since our initial temperature was not low enough.

α relaxation

The isochronous curves $\epsilon'(T)$ and $\epsilon''(T)$ are plotted in **Figure 3** for two frequencies, 10 Hz and 10^5 Hz, as an example. In blank PVDF, the first relaxation α

appears in the low temperature range, from -40 °C to -10 °C at 10 Hz, and it is observed as a step in $\epsilon'(T)$ and as a peak centered around -30 °C in $\epsilon''(T)$ at 10 Hz, being at higher temperatures for 10^5 Hz. In order to show the influence of CNT functionalization on the dielectric relaxation, we have chosen filler concentrations below the percolation threshold, when the composites show a reduced contribution of the conductivity term. Percolation thresholds are approximately 1, 5 and 3 wt% respectively for SWCNT/PVDF, SWCNT-NIT/PVDF and SWCNT-PFO/PVDF composites (see the “percolation threshold” section). Inside the concentration range below the threshold, we have chosen the maximum measured concentration to observe the effects in the best possible way. Therefore, **Figure 3** depicts the isochronal curves for SWCNT-1/PVDF, SWCNT-NIT-5/PVDF and SWCNT-PFO-3/PVDF composites. In these composites, the temperature region in which the α relaxation appears is nearly identical and the band maximum in $\epsilon''(T)$ curves is shifted by less than 3 degrees, so changes in T_g provoked by SWCNT fillers should be small, in agreement with previous results [11]. In composites with filler concentrations above the percolation threshold, AC conductivity is predominant, and it will be discussed later.

In order to further analyze the α relaxation, isothermal curves $\epsilon''(f)$ are plotted in **Figure 4** and fitted to an HN contribution (Eq. 1) for the dielectric term plus a conductivity contribution with a frequency dependence (Eq. 2). For blank PVDF, the following characteristics are observed as the temperature increases: i) an increase in the relaxation strength, ii) a peak sharpening and iii) an increase in the asymmetry, with the respective Eq. 1 parameters ranging from $\Delta\epsilon = 3.7$, $\alpha = 0.24$, $\beta = 1$ at -40 °C to $\Delta\epsilon = 4.7$, $\alpha = 0.64$, $\beta = 0.39$ at -10 °C (**Figure 4a**). The behavior is similar to that observed by Sencadas et al. [37], except for the relaxation strength, which remained nearly constant at $\Delta\epsilon = 5.2$ in their study. The HN fit also provides information about the relaxation time

τ_{NH} . **Figure 5a** shows the temperature evolution of τ_{NH} in an Arrhenius-type plot, which allows the calculation of an apparent activation energy $E_{app} = 1.11$ eV for unfilled PVDF. Such a value is similar to others obtained by the dielectric relaxation spectroscopy (DRS) technique: $E_{app} = 1.08$ eV [38], 1.05 eV [39]. However, the narrow temperature range of the α relaxation does not allow us to observe the real non-Arrhenius behavior associated to the glass transition. As it was clearly described by Kaszynska et al. [40] using nuclear magnetic resonance (NMR), dielectric and mechanical data, the complete temperature dependence of τ_{NH} can be well fitted to a Vogel-Tamman-Fulcher law. In Sencadas [37], the non-Arrhenius behavior was also apparent just by DRS, as the temperature range valid for τ_{NH} calculation resulted to be wider than in our measurements.

In order to study the influence of carbon nanotubes on α relaxation from $\varepsilon''(f)$ plots, it is necessary to separate the conductivity from dielectric contributions. This separation can be only performed if AC conductivity is not predominant, i.e. in all the composites with SWCNT concentrations above the percolation threshold. **Figures 4b** and **4c** show the evolution of $\varepsilon''(f)$ spectra after subtracting the conductivity term in SWCNT-NIT-5/PVDF and SWCNT-PFO-3/PVDF respectively. The results point out that the incorporation of carbon nanotubes into PVDF introduces some small changes in the α relaxation. Firstly, the relaxation strength increases, reaching a maximum value of $\Delta\varepsilon = 1.6$ at -10 °C, whereas $\Delta\varepsilon = 0.9$ in the neat PVDF. Analogous changes occur for the rest of temperatures at which α is present. This behavior is in the line of the increments arisen in the α relaxation region of the $\varepsilon'(T)$ plot (**Figure 3**). The increase in $\Delta\varepsilon$ could be associated to the decrease in crystallinity, which is close to 10 % (**Table 2**) and is given by an increase in the amount of the free amorphous chains involved in α relaxation. Another effect of SWCNT fillers is a small shift in the frequency of the ε'' maximum, which implies that the relaxation time τ_{NH} becomes shorter in composites. **Figure 5a** reflects the

Arrhenius behavior of τ_{NH} with activation energies around 1.0 eV in SWCNT-NIT/PVDF and 0.90 eV in SWCNT-PFO/PVDF. These results would indicate a higher molecular mobility in the amorphous domain and therefore a reduction in T_g , as it was confirmed by Anson-Casaos et al. by dynamical mechanical analysis (DMA) [24].

α_c relaxation

The other relaxation α_c appears in the 10-80 °C range both in the neat PVDF and in the composites. This relaxation feature was described for the first time by Kakutani et al. [41] and later by [24, 42, 43] using DMA. However, the α_c relaxation has seldom been analyzed in detail by DRS: the relaxation does appear neither in Sencadas et al. [37] nor in Yuan et al. [44] works, whereas in other studies its presence is only detected at the lowest frequencies or it is overlapped with the α relaxation [39, 42, 45, 46], and therefore it does not allow to obtain reliable parameter fittings.

The two-contribution model considering HN relaxation and AC conductivity remains valid. The outcomes for virgin PVDF show that the relaxation strength of α_c is nearly constant with a slight increase from $\Delta\epsilon = 4$ at 15 °C to $\Delta\epsilon = 5$ at 80 °C. According to Mijovic et al. [47], the trend does not continue above 80 °C, and the peak magnitude undergoes a decrease with temperature up to its disappearance at around 177 °C, caused by the crystalline origin of the α_c relaxation. The fitting process in our data gave shape parameters around $\alpha = 0.5$ and $\beta = 1$ for all the isothermal spectra. The Arrhenius plot of τ_{NH} gave a straight line with $E_a = 0.92$ eV, which is lower than 1.2 eV obtained in [39] and similar to 0.95 eV obtained by Mijovic et al. [47] and 0.93 eV by Linares et al. [48], thus confirming the Arrhenius character of the α_c relaxation for neat PVDF.

CNTs induce a strong increase in the α_c dielectric strength in the studied temperature range, from $\Delta\epsilon = 1$ at 15 °C to $\Delta\epsilon = 7$ at 80 °C in SWCNT-NIT5/PVDF, and from $\Delta\epsilon = 4$ to $\Delta\epsilon = 10$ in SWCNT-PFO-3/PVDF. These changes are accompanied by

increases in symmetry and broadness. **Figure 5b** shows the temperature dependence of τ_{NH} in an Arrhenius plot, whose points do not follow strictly a straight line. Data fitting to an Arrhenius behavior gave $E_a = 0.8\text{-}0.9$ eV for the composites, just a little lower than the values obtained for α relaxation. However, the SWCNT presence notably increases the α_c relaxation times of PVDF, in agreement with observations for PVDF/PMMA blends after the addition of 1 wt.% of MWCNTs [36]. The effect can be associated to the interaction between the fillers and the matrix, which affects the mobility of the chains.

The mechanism involved in α_c relaxation, according to NMR data by McBrierty et al. [49], is associated to motions of folded chains on the surface of crystal lamellae, which are more restricted than those undergone by amorphous chains. The relaxation times obtained in α_c relaxation, which are two orders of magnitude slower than in α relaxation, support that explanation. From DMA measurements, Alves et al. [43] found some effects of thermal treatments on α_c and α relaxations. The conclusion was that α_c relaxation is related to the annealing process suffered by the samples. In order to deepen in this aspect, we carried out a thermal cyclic process which consisted of one heating process from -45°C to 185°C followed by a cooling process at $10^\circ\text{C}/\text{min}$ up to -45°C and a second heating process. The results of α_c relaxation before and after the second melting process were quite similar, with only a 15 % variation in the relaxation strength. Such a small change could be related to changes in the specimen shape inside the measurement space or to changes in the degree of crystallinity.

Dielectric constant and loss tangent

The presence of CNTs significantly affects the PVDF dielectric constant (ϵ'). **Table 3** shows the ϵ' values together with the loss tangent ($\tan \delta$) at two frequencies (1 Hz and 10^5

Hz) and two temperatures (25 and 150°C) for two materials of each composite group with concentrations below and above their respective percolation thresholds.

At a low frequency (1 Hz), the dielectric constant changes from $\varepsilon' = 12$ for PVDF to $\varepsilon' = 124$ for SWCNT-1/PVDF. The rise in the dielectric constant has its origin in the presence of conductive nanofillers, which contribute to the formation of a randomly distributed network of nanocapacitors, increasing the material polarization via the Maxwell-Wagner-Sillars mechanism [50]. When the filler concentration is near the percolation threshold, nomadic charge carriers are blocked at the interfaces between CNTs and the matrix [50]. In our measurements, the effect is much less pronounced for the composites with functionalized SWCNTs, even at higher filler concentrations. Dielectric constants reach $\varepsilon' = 22$ and $\varepsilon' = 14$ respectively for SWCNT-PFO-3/PVDF and SWCNT-NIT-5/PVDF, which still have filler concentrations well below their respective percolation thresholds. The difference between both composites might be associated to the different dipolar contribution of the functional groups. At the highest frequency (10^5 Hz), the influence of SWCNTs in the dielectric constant is lower than at 1 Hz. Values change from $\varepsilon' = 9.4$ for PVDF to $\varepsilon' = 21$ for SWCNT-1/PVDF and ε' around 15 for the composites with functionalized CNTs. Whilst interfacial polarization is predominant at low frequencies, the mechanism of PVDF dipolar polarization could prevail at the moderately high frequency regime around 10^5 Hz.

Table 3 also reflects the strong increase in the dielectric constant of the composites when the CNT concentration just exceeds the percolation, reaching at 10^5 Hz values of $\varepsilon' = 105$, 50 and 43 for SWCNT-2/PVDF, SWCNT-PFO-4,6/PVDF and SWCNT-NIT-7/PVDF, respectively. In any case, the values are still very far from the $\varepsilon' = 600$ of SWCNT-3/PVDF, which is a composite with a concentration clearly above the percolation. These strong increases are in agreement with the critical behavior of the

dielectric constant near a percolation threshold of a heterogeneous system, in particular in CNT/PVDF composites [51, 52]. The concentration dependence typically follows the law $\varepsilon' \sim (\Phi_c - \Phi)^{-q}$, where Φ_c is the critical concentration at the percolation threshold, Φ the concentration of CNTs and q a scaling constant [53]. In the present work, the limited number of concentrations in the sample series does not allow to calculate the exact value of the percolation critical concentration Φ_c .

Another characteristic of the dielectric constant is the presence of the “wave” effect, which is defined as the appearance of a maximum in the isochronous curve $\varepsilon'(T)$. This phenomenon was observed by Li et al. [54] in the neat PVDF matrix and also in MWCNT/PVDF composites. In our work, the effect is only observed in SWCNT-X/PVDF composites at temperatures around 100 °C (see SWCNT-1/PVDF curves in **Figure 3a**). Following Li et al. [54], the decrease in ε' at around 100°C occurs when the semi-crystalline polymer changes into a rubbery state, making easier for the fillers to connect with each other. A decrease in the density of individual interfaces between the nanofiller and the matrix is induced and consequently a decrease in the interfacial polarization occurs. In a certain way the effect is reminiscent of the decrease of ε' when CNTs concentration surpasses Φ_c . In our data, the wave effect is hindered by CNT functionalization, possibly due to the different separation, in terms of filler wt.%, of the chosen specimens from their respective percolation threshold.

Regarding the loss tangent, Table 3 reflects that SWCNTs cause a strong increase at concentrations above the percolation threshold. The addition of untreated SWCNTs, even at relatively low amounts, leads to an increase in $\tan\delta$, from 0.07 for neat PVDF to 1.16 for SWCNT-1/PVDF at 1 Hz and 25°C, while higher amounts of functionalized SWCNTs can be added with only small changes in $\tan\delta$. A qualitative difference exists between the untreated and functionalized SWCNT composites, since $\tan\delta$ values for

functionalized SWCNT composites are systematically lower when they are compared under identical conditions (above or below the percolation threshold, constant temperature and frequency). For composites with functionalized SWCNTs below the percolation threshold (SWCNT-PFO-3/PVDF and SWCNT.NIT-5/PVDF) the loss tangent remains near that of blank PVDF, while certain increments in the dielectric constant are registered at once. The effect might be related to the role of functional groups as protective insulating layers, which hinder charge losses through the SWCNT network. Moreover, the fluoroalkyl moiety shows a somewhat greater effect than the oxygen functional groups inserted by the nitric acid treatment.

Electrical conductivity

When the electrical conductivity (σ) becomes relevant in insulating materials, the analysis of experimental data can be done through the $\log \sigma$ vs. $\log \omega$ representation. This plot provides a horizontal straight line for the frequencies in which the direct current (DC) conductivity is predominant and a dispersion region above a critical frequency ω_c , where the conductivity increases with frequency according to equation 3:

$$\sigma(\omega) = \sigma_{dc} + \sigma_{\omega} \omega^s \quad (Eq\ 3)$$

where σ_{dc} is the frequency-independent DC conductivity, σ_{ω} is a constant and s a parameter that takes values of $0 < s < 1$. **Figure 6** shows the $\log \sigma$ vs. $\log \omega$ for the PVDF matrix and the SWCNT/PVDF composites at room temperature and 150 °C. Continuous lines in the figures represent fittings to Equation 3. The outcomes reflect that conductivity increases with temperature and most especially with CNT addition.

DC conductivity analysis

Concerning the influence of temperature in the neat PVDF resin, an increase of three orders of magnitude in DC conductivity, from 10^{-11} S/m to 10^{-8} S/m, occurs when the temperature increases from 25 °C to 150 °C. In the range of 125-150 °C, where the presence of relaxations does not predominate in ε'' and consequently $\sigma(\omega)$ follows the behavior given by Equation 3, the as calculated σ_{dc} follows an Arrhenius behavior (**Figure 7**), with an activation energy close to $E_a = 1.66$ eV for the incidental charge carriers of this polymeric resin.

The effect of SWCNT incorporation on the PVDF electrical conductivity is notable (**Figure 6**). For non-functionalized SWCNTs, a transition to a conductor state occurs at a concentration of 1-2 wt%, according to a percolation mechanism. At 2 wt% SWCNTs, DC conductivity reaches a maximum value of 10^{-2} S/m, meaning an increase of almost nine orders of magnitude with respect to the insulating matrix. At higher filler concentrations, the conductivity levels off. The percolation behavior is also characterized by a significant shift of the critical frequency ω_c , from 30 Hz for 1 wt% concentration to around 10^6 Hz for 3 wt%. Such an effect is typical in disordered systems and usually follows a scaling power law dependence [55].

The incorporation of nanofillers also introduced other changes in the PVDF conductivity behavior. **Figure 7** shows that σ_{dc} still follows an Arrhenius fashion in the temperature range where it is possible to clearly define it, but the activation energies decrease, compared to neat PVDF. In fact, the E_a value changes with the addition of SWCNTs from 1.66 to 0.62 eV. On the other hand, the nitric acid treatment does not further modify E_a , while it increases to $E_a = 1.25$ eV for SWCNT-PFO composites.

AC conductivity parameters

In order to analyze the mechanisms involved in the conductivity, we calculated the exponent s of the Equation 3. **Figure 8** depicts the $\sigma(\omega)$ curves of the composites that fulfil two conditions: i) the dielectric behavior is not relevant at the chosen temperature range (-75 °C to 150 °C), and ii) the dispersive $\sigma_{\omega}\omega^s$ term is appreciable in the measured frequency range (0.1 Hz to 10^5 Hz). Both conditions are simultaneously fulfilled by the following materials: SWCNT-1/PVDF, SWCNT-PFO-4/PVDF and SWCNT-NIT-5/PVDF. These composites are just in the middle way of the insulating-conductor transition with respect to the filler concentration. Here the values of the s parameter of Equation 3 indicate the nature of the conducting 3D clusters: s -values around 0.58 are related to anomalous diffusion in fractal clusters [56] and $s = 0.72$ indicates intercluster polarization [53]. In the composite with the untreated SWCNT nanofiller, the s -exponent ranges from 0.81 at -75 °C to 0.76 at 150 °C, indicating a behavior close to the intercluster polarization model. The decrease with the temperature does not appear in composites with SWCNT-NIT, whereas in SWCNT-PFO-4/PVDF the values change from 0.72 at -25 °C to 0.64 at 150 °C, close to the diffusion in fractal cluster behavior. This trend is similar to that previously found by Ezquerro et al. [25] in SWCNT/PVDF composites, although in that report the s -value was calculated for nanofiller concentrations above the percolation concentration at a constant temperature. From our analysis, it can be additionally pointed that the increasing temperature activates an interparticle conduction mechanism in the composite, which is reminiscent of the above-commented “wave” effect in the dielectric constant $\varepsilon'(T)$.

Percolation threshold

Figure 9 compares the conductivity at two different frequencies, 0.1 Hz and 10^5 Hz, and two temperatures, 25 and 150°C, as a function of the nanofiller concentration.

Figure 9a shows data at 25°C and 0.1 Hz, in which we can observe that the influence of functionalized SWCNTs on conductivity follows a similar qualitative fashion to that generated by the incorporation of non-functionalized SWCNTs in the PVDF matrix. A percolation effect is observed in the three composites with the filler addition until reaching a maximum value of conductivity. However, in both the studied surface functionalization methods, the percolation threshold was higher than for non-functionalized SWCNTs, around 4 wt% for SWCNT-PFO and 6 wt% for SWCNT-NIT. The shift of the percolation threshold with SWCNT functionalization might be associated to several nanostructural phenomena: i) the functional groups may act as a coating layer on SWCNT surfaces [51]; ii) the electrical conductivity of individual SWCNTs may be locally hindered by surface functionalization due to the new chemical bonds; and iii) the SWCNT aspect ratio may decrease with chemical functionalization by oxidative breaking or aggregation induced by specific interactions between the functional groups [57, 58]. Apart from the percolation threshold shift, the outcomes indicate that the maximum attained conductivity was around 4×10^{-3} S/m regardless the surface modification undergone by SWCNTs. Therefore, once the electrical contact is established among the SWCNTs, the final conductivity is defined by the network characteristics but not by the intrinsic SWCNT properties. According to Ezquerro [25] this behavior can be extended to other carbon nanofillers above their respective percolation concentrations. The percolation critical concentration Φ_c typically follows the trend $\sigma \sim (\Phi - \Phi_c)^t$, where t is a critical exponent, in the framework of the generalized percolation theory for CNTs in composite materials [59]. As above commented for the $\varepsilon'(\Phi)$, the short number of specimen concentrations does not allow a calculation of an exact value for ϕ_c in the present work.

Figures 9b and **9c** respectively show the effect of frequency and temperature on the percolation threshold. The percolation at all the frequencies and temperatures occurs at

nearly identical filler contents. However, the conductivity variation across the percolation threshold at high frequencies and temperatures is not as relevant as it is in **Figure 9a**. For instance, the conductivity at 10^5 Hz and 25°C increased only by three orders of magnitude with respect to the neat polymer.

CONCLUSIONS

In the present work, SWCNT/ α -PVDF composites are comprehensively characterized by dielectric relaxation spectroscopy (DRS). The influence of the SWCNT filler and the SWCNT chemical functionalization on the PVDF dielectric behavior and AC conductivity is described.

The α relaxation for the neat PVDF and all the composites appears in the temperature range of -40 to -10°C, and the fillers induce a small increase in the relaxation strength, which can be associated to a 10% decrease in crystallinity and a decrease in the relaxation time. The α_c relaxation appears for the neat PVDF and the composites between 10-80°C. The SWCNT fillers produce a strong increase in the α_c dielectric strength, symmetry, broadness and the relaxation time.

The presence of SWCNT fillers greatly increases the dielectric constant ϵ' and the dielectric loss ($\tan\delta$) at filler concentrations above the electrical percolation threshold. Below the percolation, composites with functionalized SWCNTs demonstrate a moderate increase in ϵ' with negligible changes in $\tan\delta$. Accordingly, composites below the percolation threshold may find application in capacitive systems while composites above the percolation threshold are known to be useful in electromagnetic shielding. The “wave” effect is observed in the ϵ' (T) plot of non-functionalized SWCNT composites. The electrical percolation threshold changes with the filler functionalization, and it is maintained in the whole measured temperature and frequency range. The maximum

electrical conductivity above the percolation threshold is nearly identical ($\sim 10^{-2}$ S/m) for all the SWCNT fillers, temperatures and frequencies.

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FIGURE CAPTIONS

Figure 1. XRD (left) and DSC (right) profiles for: (a) PVDF, (b) SWCNT-2/PVDF, (c) SWCNT-PFO-4.6/PVDF, and (d) SWCNT-NIT-7/PVDF.

Figure 2. 3 D representation showing the frequency/temperature dependence of PVDF: (a) real dielectric constant ϵ' and (b) loss dielectric constant ϵ'' .

Figure 3. Isochronal curves of the complex dielectric constant, ϵ' and ϵ'' , at 100 Hz (a,b) and 10^5 Hz (c,d) respectively, for raw PVDF and composites below the percolation concentration.

Figure 4. Isothermal curves of ϵ'' spectra corresponding to the α relaxation from -40 °C to -10 °C (left) and α_c relaxation from 15 °C to 75 °C (right) of a) PVDF b) SWCNT-NIT-5/PVDF and c) SWCNT-PFO-3/PVDF composites after subtracting the conductivity term. Solid lines correspond to the HN fit.

Figure 5. Temperature dependence of the Havriliak-Negami relaxation time for the processes in PVDF and in SWCNT/PDF composites: a) α relaxation and b) α_c relaxation. Continuous lines represent Arrhenius fittings.

Figure 6. Frequency dependence of the conductivity $\sigma(\omega)$ measured at room temperature and 150 °C for virgin PVDF and their composites: a) SWCNT-X/PVDF, b) SWCNT-NIT-X/PVDF and c) SWCNT-POF-X/PVDF

Figure 7. Temperature dependence of σ_{dc} for the different SWCNT/PVDF composites. Continuous lines represent Arrhenius fittings.

Figure 8. Frequency dependence of the AC conductivity for various SWCNT/PVDF composites at different temperatures: -75, -25, 0, 25, 75, 100 and 150 °C.

Figure 9. Percolation effect in the SWCNT/PVDF composites at different temperatures and frequencies: a) 0.1 Hz and 25 °C, b) 10^5 Hz and 25 °C and c) 0.1 Hz and 150 °C.

Table 1. SWCNT/PVDF composites studied in this work apart from the blank PVDF resin

Composites	Reinforcement concentration (X= wt%)	Carbon nanotubes functionalization
SWCNT-X/PVDF	1, 2, 3	Neat
SWCNT-NIT-X/PVDF	2, 5, 6, 7, 10	Nitric acid treatment
SWCNT-PFO-X/PVDF	1, 3, 4, 4.6	Heptadecafluorooctyl phenyl groups

Table 2. DSC and XRD data for the virgin PVDF material and three selected SWCNT/PVDF composites: T_m = melting temperature, $\Delta_m H$ = melting enthalpy, T_c = crystallization temperature, $\Delta_c H$ = crystallization enthalpy, and X = crystallinity.

Material	T_m [°C]	$\Delta_m H$ [J g ⁻¹]	T_c [°C]	$\Delta_c H$ [J g ⁻¹]	X_{DSC} [%]	X_{XRD} [%]
PVDF	160.3	-42.4	122.8	39.1	40.5	40.0
SWCNT-2/PVDF	162.3	-39.6	137.6	34.0	37.8	33.7
SWCNT-PFO-4.6/PVDF	161.4	-38.9	135.5	34.9	37.2	36.3
SWCNT-NIT-7/PVDF	161.2	-36.7	135.4	33.2	35.1	29.6

Table 3. Dielectric constant and loss tangent at two different frequencies, 1 Hz and 100000Hz, and temperatures, 25 °C and 150 °C, corresponding two composites below and above the critical percolation concentration in each group.

Material/Frequency-Temperature	1 Hz- 25 °C		10 ⁵ Hz-25 °C		1 Hz-150 °C		10 ⁵ Hz-150 °C	
	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$	ϵ'	$\tan \delta$
PVDF	12	0.07	9,4	0.04	29	4.1	11	0.06
SWCNT-1/PVDF	124	1.16	21	0.16	192	7.6	24	0.2
SWCNT-2/PVDF			105	4.11	5597	16687	85	8
SWCNT-PFO-3/PVDF	22	0.07	16	0.06		6.1	20	0,1
SWCNT-PFO-4.6/PVDF	262	20370	50	1.39		1901	68	2
SWCNT-NIT-5/PVDF	14	0.07	13	0.04		6.5	15	0.07
SWCNT-NIT-7/PVDF	388	254	43	0.59		212	58	0.63

FIGURE 1. XRD (left) and DSC (right) profiles for: a) PVDF, b) SWCNT-2/PVDF, c) SWCNT-PFO-4.6/PVDF, and d) SWCNT-NIT-7/PVDF

FIGURE 2. 3 D representation showing the frequency/temperature dependence of PVDF: a) real dielectric constant ϵ' . b) loss dielectric constant ϵ'' .

FIGURE 3. Isochronal curves of the complex dielectric constant, ϵ' and ϵ'' , at 10 Hz (a,b) and 10^5 Hz (c,d) respectively, for raw PVDF and composites below the percolation concentration.

FIGURE 4. Isothermal curves of ϵ'' spectra corresponding to the α relaxation from -40 °C to -10 °C (left) and α_c relaxation from 15 °C to 75 °C (right) of a) PVDF b) SWCNT-NIT-5/PVDF and c) SWCNT-PFO-3/PVDF composites after subtracting the conductivity term. Solid lines correspond to the HN fit.

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FIGURE 9. Percolation effect in the SWCNT/PVDF composites at different temperatures and frequencies: a) 0.1 Hz and 25 °C, b) 10^5 Hz and 25 °C and c) 0.1 Hz and 150 °C.

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