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Drastic modification of the piezoresistive behavior of polymer nanocomposites by using conductive polymer coatings

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Abstract

We obtained highly conductive nanocomposites by adding conductive polymer poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT/PSS)-coated carbon nanotubes (CNTs) to pristine insulating Polycarbonate. Because the PEDOT/PSS ensures efficient charge transfer both along and between the CNTs, we could attribute the improvement in electrical conductivity to coating. In addition to improving the electrical conductivity, the coating also modified the piezoresistive behavior of the nanocomposites compared to the material with pristine uncoated CNTs: whereas CNT/Polycarbonate samples exhibited a very strong piezoresistive effect, PEDOT/PSS-coated MWCNT/Polycarbonate samples exhibited very little piezoresistivity. We studied this change in piezoresistive behavior in detail by investigating various configurations of filler content. We investigated how this observation could be explained by changes in the microstructure and in the conduction mechanism in the interfacial regions between the nanofillers. Our study suggests that tailoring the piezoresistive response to specific application requirements is possible.

Keywords: A. Carbon nanotubes, B. Polycarbonate, C. Piezoresistivity, D. Conductivity, E. Conductive polymer

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1. Introduction

The preparation of conductive filler/polymer composites is currently an active field of research that is motivated by the large number of applications that require polymer materials with high electrical conductivity. Carbon nanotubes (CNTs) are considered to be good candidate for conductive fillers because their high aspect ratio allows percolation at very fraction of fillers. The material becomes conductive from a macroscopic point of view when, at a sufficiently high filler concentration, a percolated network is created throughout the sample.

Conductive filler/polymer nanocomposites can be understood as an interconnected network of electrically conductive particles that are embedded in an insulating medium. In such nanocomposites, the effective electrical conductivity of the whole percolated network is mainly dominated by the conductivity of the junctions between the CNTs [1, 2]. As the polymer matrix is a dielectric, charge transfer can take place by tunneling [3] when the CNTs are close to each other. Simmons [3] described the equivalent resistance associated with the tunneling transfer mechanism between two conducting electrodes (here the CNTs). The magnitude of the tunneling resistance increases exponentially with the separation of the electrodes, yet tunneling can exist only when the CNTs are very close to each other (1.8 nm is usually considered to be a cut off distance above which the effective resistance of the tunneling junction is so high that charge transfer is not possible) [4, 5, 6]. The direct consequence is that most CNT-based nanocomposites exhibit intense piezoresistive behavior, leading several research groups to design nanocomposite-based strain sensors [7, 6, 8, 5, 9].

In strain sensing applications, the piezoresistive response of nanomaterials is desirable. However, this response requires improvement over the available response in the existing devices. Indeed, several limitations have been observed. For example, the nanocomposites described in [6] and [10] exhibit non-linear piezoresistive behavior, strong deviations between elastic and plastic regimes and sensitivity to inelastic deformation and material degradation. These factors are key limitations for designing sensors, which should be able to return highly repetitive measurements.

Highly conductive nanocomposites may also be required in other applications, but without strong piezoresistive behavior. Applications such as flexible electronics would indeed require

that the conductivity remained as constant as possible when the material experienced strain. A challenge is to produce nanocomposites that display both (1) high electrical conductivity and (2) reduced, reversible and linear piezoresistivity.

Because strong and non-reversible piezoresistive behavior directly results from the high sensitivity of the tunneling resistance of the CNT-to-CNT junctions, one possible way to meet this challenge is to replace the tunneling with a less strain-dependant mechanism. In this study, we investigate the piezoresistive features of Polycarbonate (PC) nanocomposites using CNTs coated with poly(3,4-ethylenedioxy-thiophene) poly(styrenesulfonate) (PEDOT/PSS), a well-known conductive polymer in flexible electronics. Previous work on this material [11] showed that multi-walled CNTs (MWCNTs) coated with 1.3 weight ratio of Ethylene Glycol-treated PEDOT/PSS (EPP) had a diameter that was around three times larger than that of uncoated MWCNTs. The highly conductive polymeric layers merge at the CNT junctions to exchange the original tunneling conduction with the conductive network of EPP. It is thus reasonable to expect that these samples would exhibit different piezoresistive effects.

Our objective in this paper is to compare the piezoresistive behavior of MWCNT/PC (CNT/PC) and EPP-coated MWCNT/PC (E-CNT/PC) nanocomposites under both mechanical and thermal loading and to correlate their responses to the initial microstructure and/or to the evolution of this microstructure. Section 2 describes the synthesis of the nanocomposites and the experimental protocol used to probe the piezoresistive behavior of these samples. In Section 3, we describe the influence of the conductive polymer network on the piezoresistive effect during both mechanical and thermal loading as well as on the damage and time-dependent mechanical properties of the nanocomposites. These results clearly highlight the potential of this approach to tune the piezoresistive response of such materials.

2. Materials and methods

2.1. Description of raw constituents

Polycarbonate in fine granular form (LexanTM ML9103-111T) was provided by SABIC Innovative Plastics. Carboxyl(-COOH) functionalized MWCNTs were purchased from Cheap-Tubes, Inc. Thermogravimetric analysis of as-received MWCNTS confirmed the presence of 2.15 ± 0.15 wt% -COOH functional groups. According to the manufacturer, the diameter

of the cross-sectional area is 8-15 nm and the length is in the range of 10-50 μm . This was confirmed by TEM observations as shown in Figure 1(a). PEDOT/PSS in aqueous dispersion (Clevios PH1000) was purchased from HC Starck, Inc. The initial concentration of PEDOT/PSS was 1.3 wt% and the ratio between PEDOT and PSS was 1:2.5 by weight. Ethylene glycol (EG), dichloromethane (DCM) and dimethylformamide (DMF) were purchased from Sigma-Aldrich.

Figure 1: (a) TEM image of pristine MWCNTs; (b) TEM image highlighting the EG-PEDOT/PSS coating and interconnections on MWCNTs.

2.2. Sample preparation

CNTs were first coated with highly conductive EG-treated PEDOT/PSS (abbreviated hereafter as EPP) via a solution process. The complete procedure is detailed in [11]. First, 5 wt% EG was added to the PEDOT/PSS solution and the mixture was stirred for 12 h at 80 °C until 50% of the solution mass had evaporated. Then, 2.0 wt% MWCNTs were added to 10 ml of the condensed EPP solution. The solid weight ratio between EPP and MWCNT was estimated to be 1.3:1. We previously demonstrated [11] that the thickness of the conductive polymer coating on the CNTs is directly related to the EPP-to-MWCNT weight ratio used during the process. With the 1.3:1 configuration used here, the thickness of the coating measures around 10 nm. We expect that thickness to be enough to ensure bridging between the CNTs at a larger scale than the classical tunneling effect. Next, we exfoliated the MWCNTs using a Brason 8510 bath sonicator (Thomas Scientific) for 1 h, followed by an Ultrasonic processor (Cole-Parmer) at 20 kHz and 500 W for 15 min in an ice bath to prevent extensive heating and damage of the MWCNTs.

EPP-coated MWCNTs (E-CNT), shown in Figure 1(b), were added to a solution of 3 g of polycarbonate dissolved in 25 g of DCM, prepared by stirring PC into the DCM for 5 h at room temperature. Three different configurations were produced according to the MWCNT content with respect to PC: 1.0, 1.5 and 2.0 wt%. The resulting mixtures of E-CNT/PC were stirred for 12 h at room temperature. Thin film samples were then prepared via a cast coating method. The casted films were formed into 0.25 ± 0.05 mm-thick rectangular disks by a hydraulic hot press (Pinette Emidecau Industries) at 240 °C and 7 bar pressure for 30

min. Just before hot pressing, the films were heated for 30 min until the temperature reached 240 °C. The samples were then cooled with no change in pressure and at a cooling rate of 6 °C/min.

The corresponding configurations of CNT/PC nanocomposites were also prepared by this method except that the exfoliation of the MWCNTs was performed in a DCM solution. The parameters of the ultrasonic processor remained the same. These samples were used to study the effect of the MWCNT concentration and to investigate the effect of the PEDOT/PSS coating. We limited the study to configurations that were above the percolation threshold. Samples with a lower MWCNT content, in which the electrical resistance was not driven by interparticle resistance, were not studied as they were not of practical interest. A summary of the composition and volume resistivity of the samples is shown in Table 1.

Table 1: Composition of PC nanocomposites.

2.3. Characterization techniques

The thin films were cut into rectangular coupons with the dimensions 90 mm $\pm$ 0.5 mm x 10 mm $\pm$ 0.5 mm for electromechanical testing. To increase friction with the testing machine grips and electrically insulate the samples from the testing device, the coupons were fitted with 20 mm-long adhesive sandpaper tabs. Two copper wires were attached to the surface of the samples and glued with silver paste to ensure good electrical contact. Then, the electrode surface was coated with epoxy glue for both electrical insulation and to prevent the electrodes from peeling off during the test. The distance between the electrodes was 40 mm. All dimensions of the specimen are provided in Figure 2(b). The samples were carefully positioned in the grips to ensure that the electrodes were insulated from the testing device and correctly centred and aligned.

Figure 2: (a) Sample of a coupon for mechanical testing; (b) Details and dimensions; (c) A coupon mounted on the testing device; (d) The test profile shows a series of loading/unloading cycles at a rate of 1 mm/min with an incremental displacement of 0.3 mm.

Specimens were tested using an Instron 5882 universal tensile machine (UTM) equipped

with a 500 N load cell. The test consisted of a series of loading and unloading cycles at a rate of 1 mm/min (Figure 2(d)). Succeeding cycles increased the displacement by 0.3 mm with respect to the previous one. The reasons for this type of testing were twofold: (1) to analyze the evolution of the piezoresistive effect by measuring the gauge factor and the residual change in resistance after every loop and (2) to identify the corresponding microstructural changes by measuring the change in the stiffness of the samples. The measurement of longitudinal strain was accomplished via an Instron video extensometer attached to the UTM that tracked the longitudinal position of the two white dots painted on the surface of the sample; the strain gauge was defined by marking two dots 25 mm apart along the longitudinal axis. The electrical resistance of the samples during the mechanical test was measured using an Agilent U2741A digital multimeter. In our set up, the current was injected by a pair of leads connected to the electrodes; a second pair of leads was used to measure the electrical resistance. For all configurations, at least five samples were tested. The results show a representative example.

The thin films were cut into smaller coupons with dimensions of about $15 \text{ mm} \pm 0.5 \text{ mm} \times 6 \text{ mm} \pm 0.3 \text{ mm}$ and connected with copper wires as described previously for the measurement of the temperature dependent DC electrical resistance. The distance between the electrodes was $9 \text{ mm} \pm 0.5 \text{ mm}$. The specimens were placed in a temperature-controllable chamber, which was continuously purged with N_2 , and the resistance was measured using a two-probe technique with an Agilent 1252B multimeter. The temperature ranged between 30 and 160°C with a heating rate of $5^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Piezoresistive effect

Figures 3(a) and (c) show the relative change in electrical resistance, $(\Delta R/R_0)$, with respect to the longitudinal strain, (ε) , for E-CNT/PC2.0 (with PEDOT/PSS coating) and CNT/PC2.0 (without PEDOT/PSS coating) samples, during the cyclic loading. The corresponding stress-strain curves are plotted in Figures 3(b) and (d). Note that the axes of Figures 3(a) and (c) are different. For a direct comparison, these curves are plotted together for all formulations in Figures 3(e) and (f).

The macroscopic electrical resistance displays strain dependency in both configurations; however, even at first sight, it is clear that the strain dependency is quite different. The strain dependency of the macroscopic electrical resistance of E-CNT/PC2.0 is weaker, almost linear and repeatable between cycles. The relative change in resistance, $\Delta R/R_0$, at 2.5% strain is only about 0.03. The residual change in the electrical resistance remains very small (0.005) after unloading from a 2.5% maximum strain. In comparison, CNT/PC samples show a much stronger $\Delta R/R_0$ of up to 0.19 for CNT/PC2.0 at 2.5% strain. Additionally, the residual resistance permanently increases every time the sample reaches a new maximum strain.

Figure 3: Change in electrical resistance vs tensile strain for samples with 2.0 wt% MWCNT: (a) E-CNT/PC2.0; (c) CNT/PC2.0; and (e) Both samples. Corresponding stress-strain curves from incremental cyclic curves (b) E-CNT/PC2.0 ; (d) CNT/PC2.0; and (f) Both samples.

To characterize the piezoresistivity quantitatively, we compare the behaviors of the different material formulations by measuring the gauge factor, k , and the residual change resistance during each cycle. The gauge factor can be determined as the slope between $\Delta R/R_0$ and the tensile strain, ε , such as [12]:

$$\frac{\Delta R}{R_0} = k \cdot \varepsilon. \quad (1)$$

Recall that the resistance in a bulk material with a rectangular cross-section is given by:

$$R = \frac{\rho l}{wt}, \quad (2)$$

where ρ is the volume resistivity, l is the length, w is the width and t is the thickness of the sample. Calculus of variation based on Equation 2 provides information about how the global change in resistance relates to either the change in volume resistivity or the change in geometrical features:

$$\frac{dR}{R} = \frac{d\rho}{\rho} + \frac{dl}{l} - \frac{dw}{w} - \frac{dt}{t}. \quad (3)$$

Provided we maintain the infinitesimal strain regime (which is actually possible because we never exceed 3 % tensile strain, see Figure 3), the following approximation holds: $dl/l \approx \varepsilon$ and $dw/w = dt/t \approx -\nu\varepsilon$, where ν is the Poisson ratio of the constitutive material. Substituting these values into Equation 3 and dividing the expression over the longitudinal strain, the

gauge factor, k , is defined as:

$$k = (1 + 2\nu) + \frac{d\rho}{\rho \cdot \varepsilon}. \quad (4)$$

According to Equation 4, the gauge factor accounts not only for the change in resistivity of the material but also for any geometric deformation. Knowing that the Poisson's ratio for polycarbonate is $\nu = 0.38$ [13], the geometric factor $1 + 2\nu$ thus equals 1.76. In homogeneous materials, this corresponds to the change in resistance due solely to the modification of the length and the cross-sectional area of the samples.

For all material configurations described in Table 1, the gauge factor, k , was measured over the elastic unloading section of every cycle using linear fitting as indicated schematically in Figure 3(c). Figure 4(a) shows the resulting variation in the gauge factor during every loading-unloading cycle. The x-axis corresponds to the maximum strain attained during each cycle. It was not possible to compare the curves at the highest strain levels of some samples because the addition of MWCNTs made the samples brittle.

Figure 4: (a) Change in the gauge factor; and (b) Residual change resistance with respect to the maximum strain attained in every cycle for all configurations. The dotted line corresponds to the geometric factor, $1 + 2\nu = 1.76$.

First, it should be noted that the initial gauge factor differed between the two families of samples. In the CNT/PC samples, regardless of the MWCNT concentration, k was larger than the pure geometrically induced value of 1.76 (marked as a dashed line on Figure 4(a)), whereas it was less than this value in the samples with PEDOT/PSS-coated MWCNTs. For CNT/PC samples, the k values found are consistent with those in the literature [4, 6, 8, 10, 14]. This is the first evidence that the piezoresistive behavior is largely amplified by the strain dependency on the nanocomposite's electrical volume resistivity (the term $\frac{d\rho}{\rho \cdot \varepsilon}$ in Equation 4). The initial values for the samples containing E-CNT are slightly below the geometrically induced value and remain stable. This is evidence that the electrical volume resistivity of these materials is nearly independent of the strain level and might even exhibit a slightly negative dependency.

Second, the gauge factor in samples containing E-CNT is less sensitive to subsequent strain increments. k for E-CNT/PC2.0 is very stable as it goes from $k = 1.06$ at the initial state to $k = 1.48$ at $\varepsilon_{max} = 2.5$ %. CNT/PC samples, on the other hand, display stronger

piezoresistive behavior even at low strain levels, and the piezoresistivity of these samples is considerably affected by the strain increments of each cycle. For example, within the same strain gauge mentioned before, the gauge factor for CNT/PC2.0 changes from $k = 2.76$ to $k = 5.25$. What this means is that the use of CNT/PC samples as strain sensors is limited because the gauge factor changes with respect to the loading history, whereas E-CNT/PC samples display a more constant piezoresistive effect.

Third, CNT/PC samples display strong non-reversible changes in electrical resistance, whereas EPP-containing samples display very limited irreversible changes. For example, CNT/PC2.0 undergoes a 10% increase in electrical resistance at 3% strain, whereas the permanent change in resistance in any of the E-CNT/PC samples is negligible (Figure 4(b)).

These observations (different initial gauge factors, different changes in the gauge factors with strain and different irreversible effects) testify to the fact that the conduction mechanism and the microstructure are drastically different between CNT/PC and E-CNT/PC samples.

Strong, non-linear piezoresistive behavior, like that exhibited by CNT/PC samples, has been found experimentally [7, 6, 10] and theoretically [14, 15] in materials with easily disrupted percolating network of conductive fillers embedded in a highly resistive matrix. Typically, the tunneling resistance increases exponentially with respect to separation between fillers. Some of the known microstructural features that promote strong piezoresistive behavior (and usually low electrical conductivity) are the low concentration of conductive fillers [6], the poor dispersion of fillers and nanotube agglomeration [14], the alignment of fillers in the direction of the deformation [10], and the use of fillers with small aspect ratios, such as carbon black particles [6]. We attribute the strong piezoresistive effect of CNT/PC samples to the random distribution of MWCNTs. In particular, the piezoresistive response of CNT/PC2.0 suggests a poor dispersion and possibly MWCNT aggregation. These suggestions will be confirmed in the next section when the evolution of the mechanical properties is discussed.

The modified microstructure of E-CNT/PC samples is responsible for the large difference in the resistance-strain relationship in comparison with CNT/PC samples. As was described previously [11], the microstructure of E-CNT/PC samples consists of a well-distributed network of MWCNTs embedded in a PC matrix where the MWCNTs are coated with EPP. In these samples, the weight ratio between EPP and MWCNT is fixed at 1.3:1, which corresponds to an EPP coating of around $8 \text{ nm} \pm 2 \text{ nm}$ thick. The TEM image of EG-PEDOT/PSS

coated MWCNTs shown in Figure 1(b) clearly displays the EPP coating around the nanotubes and the interconnections formed between them. Additionally, excess EPP in the form of spheres with average diameters of $67 \text{ nm} \pm 12 \text{ nm}$ are also found embedded in the PC matrix. From previous electrical conductivity characterization on these samples, it was found that the tunneling conduction mechanism had been replaced by a conductive network, with the EPP coatings of each nanotube in direct contact with each other, and where the MWCNTs act as a backbone structure in the PC matrix. The small gauge factor and its consistency throughout the cycles indicate that the nanocomposite behaves similarly to a bulk material (i.e., the resistance-strain relationship is only a function of the geometrical change, which is represented by a gauge factor value comparable to the geometric factor.) The absence of true piezoresistive behavior and of irreversible effects can be understood based on the assumption that the conduction mechanism is mainly guided by a conductive polymer bridge between the conducting nanoparticles. These PEDOT/PSS contacts at the interconnections can accommodate small amounts of longitudinal strain without significant changes in electrical resistance. In the next subsection, we examine this hypothesis by looking in detail the change in electrical resistance with respect to temperature.

3.2. Temperature-dependent resistance change

Thus far, we have shown that the difference in the resistance-strain response between the two types of nanocomposites is related to a fundamental change in the conduction mechanism. In the CNT/PC conductive network, the main resistive elements are the thin, insulating polymer barriers at CNT/CNT junctions. The resistance of these junctions is largely dependent on strain as the tunneling mechanism can take place only in very short range. In the E-CNT network, interparticle charge transfer comes from a conductive polymer bridge that completely changes the macroscopic response of the material. Here, we focus on the change in resistance with respect to temperature in both families of nanocomposites. These results provide evidence concerning the actual conduction mechanisms in each configuration.

The temperature dependence of the tunneling effect has been described since the early work of Sichel [16]. It is accepted that the main mechanism leading to resistance change with temperature is the modification of the tunneling distance caused by a mismatch in the coefficients of thermal expansion among the constituents [17, 18, 19, 20]. The results for our

samples are shown in Figure 5(a), where R/R_0 is the resistance divided by the initial value at room temperature. CNT/PC samples exhibit a negative temperature coefficient (NTC), i.e., the resistance decreases steadily with increasing temperature. NTC has been observed in nanocomposites in which the polymer matrix has a high glass transition temperature (such as PVC, $T_g = 355$ K [16] and PEEK, $T_g = 419$ K [20]). This behavior has been explained by the rearrangement of the percolated network that results in an increased number of interconnections. Alternatively, the increasing thermal energy may facilitate a conduction potential barrier jump [18]. PC is a polymer with $T_g = 420$ K; the NTC behavior of CNT/PC observed in our experiments is thus consistent with the literature.

Figure 5: (a) Relative change in resistance; and (b) Normalized electrical conductivity with respect to temperature for selected configurations.

E-CNT/PC samples display a different behavior. At first, the samples exhibit an NTC behavior (similar to CNT/PC samples). They then feature a crossover region into a positive temperature coefficient (PTC) at around $T_X = 90$ °C. The key point is that the temperature-dependent resistance of E-CNT/PC samples indicates the distinctive temperature-dependent conduction pattern of PEDOT/PSS [21, 22] albeit shifted to a higher temperature. To illustrate this, Figure 5(b) shows normalized electrical conductivity, σ/σ_{T_X} , for the E-CNT/PC samples (where σ_{T_X} is the conductivity value at the crossover temperature) in comparison with the normalized electrical conductivity of PEDOT/PSS fibers from [21].

The slight shift towards higher temperature for the transition to metallic-like conduction with respect to pristine PEDOT/PSS is probably due to the microstructure of E-CNT/PC, in which EG-PEDOT/PSS appears as a thin layer surrounding the nanoparticles within the bulk material. This is a different situation compared with bulk PEDOT/PSS fibers [21], where water and/or solvent removal is much easier. Thus, we can confirm from this evolution of global resistance with respect to temperature that the conductivity is actually guided by EPP bridges between particles and not by the tunneling effect as happens in CNT/PC samples.

3.3. Viscoelastic behavior, damage and permanent residual strain

To shed some light on the microstructural mechanisms underlying the piezoresistive effect of these nanocomposites, we observed macroscopic mechanical properties such as (1) the

initial change in **the** material stiffness due to the addition of MWCNTs, (2) the evolution of stiffness and (3) **the** residual strain after every loading-unloading cycle.

First, it is generally accepted that CNTs have the potential to increase the stiffness and toughness of polymer nanocomposites even at low CNT concentrations as long as an efficient stress-strain transfer is ensured between nanofillers. Thus, the modification of the initial stiffness is an indicator of the state of **the** dispersion and the efficiency of **the** bonding between the CNTs and the surrounding matrix. A vast number of works have reported the effect of CNTs on **the** Young's moduli of thermoplastic polymers; reviews can be found in [23, 24]. Relations between **changes** in **the** stiffness and dispersion of nanotubes **have** also been investigated in depth in [25, 26]. The initial Young's **Moduli** of the samples in this study **are** shown in Figure 6(a). Specimens containing **EPP** show a clear trend of increasing stiffness with increasing MWCNT content: up to 22% with 2.0 wt% MWCNT with respect to pure PC. On the other hand, **CNT/PC** samples can improve the stiffness of PC by **only** 18% at 1.5 wt%, and increasing MWCNT content to 2.0 wt% results in a negligible improvement **over** the original configuration. These results suggest that the dispersion state and interaction between the nanofillers and the matrix is much better for **E-CNT/PC** samples than for **CNT/PC samples** because **EPP** acts as an effective dispersing agent [27, 28]. In particular, the poor performance of **CNT/PC2.0** can be attributed to aggregation of MWCNTs and ultimately **to** an uneven state of dispersion of the nanofillers **in** the polymer matrix. It is not surprising then that **CNT/PC2.0** samples also showed the strongest piezoresistive effect among our configurations (see Figure 4(a-b)).

Figure 6: (a) Average Young's **moduli** of the samples; (b) Damage evolution; and (c) Residual strain as a function of the maximum strain during every cycle.

Secondly, the microstructural changes that are associated with the evolution of piezoresistive **behavior** also affect the mechanical properties of the material as it undergoes tensile strain. In particular, PC and PC nanocomposites exhibit softening behavior (i.e., a reduction in the apparent stiffness in each cycle) and permanent residual strain after unloading during the viscoelastic regime. These effects are also modified by the addition of nanofillers [29, 30, 31]. Previously, we reported that the addition of MWCNTs accelerated degradation mechanisms such as filler-matrix debonding in MWCNT-epoxy nanocomposites. The degra-

dation was observed macroscopically **with** the reduction of the material's apparent stiffness [32].

In a thermoplastic material like PC, softening **behavior** and permanent residual strain are the result of microstructural mechanisms that can be understood from classical viscoelastic theory. The viscoelastic response of **a** thermoplastic material may be approximated by the Burgers' or **four-parameter** model [33, 34], which results from the combination of two elements in series, a Maxwell fluid and a Kelvin solid. The strain at any time, t , can be divided in an instantaneous elastic component, ε_∞ , and two **time-dependent** components, namely the delayed elastic term, ε_K , coming from the Kelvin solid and a flow term, ε_M , from the Maxwell fluid. Therefore, a simple phenomenological model is defined as:

$$\varepsilon(t) = \varepsilon_\infty + \varepsilon_K(t) + \varepsilon_M(t) \quad \text{with} \quad (t) = \sigma \left(\frac{1}{E_0} + \frac{1}{E_1} (1 - e^{-\frac{t}{\tau}}) + \frac{t}{\mu_0} \right), \quad (5)$$

where σ is the applied stress, E_0 and μ_0 are the stiffness and the viscosity of the Maxwell spring and dashpot, respectively, E_1 and μ_1 are the stiffness and viscosity of Voigt spring and dashpot, **respectively**, and $\tau = \frac{\mu_1}{E_1}$ is the relaxation time. The elastic component is related to bond stretching in polymer molecules, which is reversible once the stress is removed. **On** the other hand, the **time-dependent** components are due to the lack of primary bonds between polymer chains, which results in their rearrangement and molecular movement as the material tries to accommodate a particular stress. These two processes occur simultaneously and are responsible for the softening behavior observed during the loading-unloading cyclic tests.

An example of **a** cyclic stress-strain curve showing measurement definitions is **presented** in Figure 3(d). This response was characterized **in** all configurations by measuring the evolution of stiffness and the residual permanent strain, ε_i^p . **To characterize** the softening behavior, we used a damage variable, d , defined as

$$d_i = 1 - \frac{E_i}{E_0}, \quad (6)$$

where E_0 is the initial **Young's** modulus and E_i is the current secant **Young's** modulus measured in every loading-unloading cycle. The damage variable, d , and the residual strain, ε_i^p , were plotted with respect to ε_{max} in Figure 6(b) and (c). The results indicate different responses among pristine PC, **CNT/PC** and **E-CNT/PC** samples1 effects due to the different

MWCNT loadings are difficult to resolve. In general, we observed that, for a particular level of strain, the addition of MWCNTs (1) decreases the damage levels and (2) increases the amount of residual permanent strain. It is also clear that E-CNT/PC samples are more effective in promoting these effects than CNT/PC samples. The possible reasons for this are (1) a better dispersion of the MWCNTs due to EPP acting as a dispersing agent and (2) a better interaction between fillers and the matrix. Indeed, it was demonstrated in [35] that PEDOT/PSS leads to an increase in the stiffness in this material because of hydrogen bondings between PEDOT/PSS and PC and the free volume reduction in the PC matrix. Therefore, despite possible additional microstructural degradation mechanisms such as debonding between MWCNTs and the matrix, the dominant mechanism is the restriction of polymer chain mobility by the MWCNTs, which preserves the stiffness of the material. This loss of mobility is also responsible for the increment in the residual permanent strain because the MWCNT network also prevents strain relaxation during the unloading stage.

4. Conclusions

Using conductive polymer-coated CNTs is a way to obtain a highly conductive material that is free of irreversible resistance changes and history-dependent piezoresistive effects. The gauge factor in E-CNT/PC samples is comparable to that of a bulk material, thus, cancelling out the true piezoresistive effect that is characteristic of other conductive filler/polymer nanocomposites. Analyses of the initial stiffness and softening behavior of these materials suggest that their microstructure consists of a well-dispersed network of MWCNTs with a redundant number of paths for electrical conductivity, where the main conduction mechanism is through direct contacts between the PEDOT/PSS coatings on the fillers. The temperature-dependent resistance also supports this conduction mechanism. As the strain increases, the E-CNT network is able to accommodate the polymer chain movements without compromising the conductive network due to the enlarged interfacial contact area between the PEDOT/PSS coating. Simultaneously, E-CNT fillers are more effective in restricting the slippage between PC chains. All this explains the weak and unchanging piezoresistive behavior of this kind of sample. A material with this behavior would be relevant in multifunctional materials in which it is desirable for the conductivity of the material to be unaffected by mechanical loads.

This material is also suitable for sensing applications because of its good linearity and its insensitivity to inelastic deformations.

On the other hand, the absence of EPP in CNT/PC samples suggests that the main conduction mechanism on the MWCNT network is the tunneling effect. The poor dispersion state creates fewer pathways for electrical conduction within the material, making these samples more sensitive to strain. This results in a stronger, exponential, and more variable piezoresistive effect. In particular, we observed that CNT/PC2.0 samples had the least effective network in terms of mechanical properties, as suggested by their low initial stiffness and weak ability to restrict softening behavior. Consequently, this sample exhibited the strongest piezoresistive effect, the largest variation of the gauge factor with respect to strain and a significant permanent increase in resistance upon unloading.

We can also conclude that there is a clear relationship between the quality of the MWCNT-network and the magnitude and variation of the piezoresistive effect: a robust, well-dispersed, highly conductive network will result in a low and stable piezoresistive effect, whereas samples with strong variable piezoresistive effects have nanofiller networks that are easily disrupted by applied strains.

We offer here a technique to tailor the piezoresistive response of highly conductive nanocomposites dependent on application requirements. Although we used carbon nanotube fillers, we believe that the concept can be extended to all formulations in which the conductive nanofillers can *a priori* be coated by a conductive polymer.

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5. References

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1

Table 1: Composition of PC nanocomposites.

Abbreviation	MWCNT loading (wt%)	EG loading in PEDOT/PSS (wt%)	EG-PEDOT/PSS loading (wt%)	Initial out-of-plane volume resistivity ($\Omega \cdot cm$) [11]
PC	0	0	0	5.1×10^{16}
CNT/PC1.0	1.0	0	0	1.03×10^8
CNT/PC1.5	1.5	0	0	4.33×10^7
CNT/PC2.0	2.0	0	0	1.8×10^7
E-CNT/PC1.0	1.0	5	1.3	4.2×10^5
E-CNT/PC1.5	1.5	5	1.95	2.3×10^5
E-CNT/PC2.0	2.0	5	2.6	1.3×10^5