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CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE (PVDF)-DOUBLE-WALLED CARBON NANOTUBES (DWNT)

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ABSTRACT

In this work, we propose a new generation of sensors and actuators based on a piezoelectric polymer (PVDF) with embedded carbon nanotubes. Polyvinylidene fluoride (PVDF)-double walled carbon-nanotubes (DWNT) composite films are prepared with the goal to develop new polymeric materials with enhanced electrical and electromechanical properties. Electrical conductivity and dielectric properties of polyvinylidene fluoride- double-walled carbon nanotubes composites are investigated as a function of frequency (10 Hz -1 MHz), and as a function of weight fraction (0.01-2 wt%). DWNT and PVDF are mixed under mechanical stirring and sonication. The dispersion is assessed by Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), indicating a good dispersion. Differential Scanning Calorimetery (DSC) is used to study the effect of DWNTs inclusions on the glass transition temperature, T_g, and the crystallinity of the resulting PVDF composite. The percolation threshold is computed by using the bulk conductivity data and it is found that percolation occurs at about 0.19wt%.

INTRODUCTION

Carbon nanotubes (CNTs) [1, 2] have been considered as ideal fillers in composites due to their low density (0.8 to 1.3 g/cm^3), high aspect ratio (~1000) and superior electrical, mechanical and thermal properties [3-6]. These properties are a result of the microstructure of the CNTs, which are hexagonal sheets of carbon atoms, rolled into a long, slender, quasi-one-dimensional cylindrical shape often capped at each end [7]. The unusual combination of properties with apparently paradoxical attributes such as high strength and modulus yet high flexibility, relatively high elongation at break, and low density, render them very unique inclusions that would allow us to improve properties of polymers yet still preserve their advantages such as ease of processing, lightweight, and flexibility. Although they were discovered almost fifteen years ago, production of CNTs has yet to overcome some important obstacles in terms of yield, availability, purity and cost. Despite that, the inherent potential suggests that further exploration is warranted. One of the challenges in developing and processing composites is the homogeneous dispersion of the inclusions in the matrix. Dispersion is an even bigger challenge in the case of CNTs because intrinsic van der waals attraction among the tubes, in combination with their high surface area and high aspect ratio, leads to significant agglomeration and clustering, thus preventing efficient transfer of their superior properties to the matrix. Although a number of studies have focused on dispersion of CNTs, complete dispersion of CNT in a polymer matrix has rarely been achieved. Over the past decade, great strides have been made in exploiting the unique combination of electronic and mechanical properties of carbon nanotubes (CNT) [8,9]. Several publications document the progress made in fabrication and characterization of CNT nanocomposites [8-10]. Unfortunately, it is difficult to draw definite conclusions about electrical conductivity from these published studies because the reported levels of CNT loading required to achieve a percolation concentration (i.e. an appreciable increase in electrical conductivity) vary widely, ranging from less than 1% to over 10%. Two reasons could account for these differences: (1) the CNT bundles are not sufficiently dispersed in the polymer matrix, and (2) experimental difficulties may result in inaccurate detection of the onset of conductivity. Difficulty in obtaining homogeneously dispersed CNT–polymer

nanocomposites arises from the non-reactive nature of the CNT surface and the unavoidable bundle formation due to van der waals attraction during synthesis. Most published work has focused on chemical modification of the CNT to improve dispersion through functionalization oxidization, melt mixing, and compounding [8]. However, successful dispersion remains elusive. The resulting bundling yields a larger effective diameter of the conductive inclusions. As a result, the aspect ratio appears reduced. The outcome is the first case where increased loading levels are required to successfully achieve percolation. In the second case, instrument sensitivity and sample preparation issues may be masking an initial percolation transition at very low loadings. Using a method developed in our laboratory [11,12], CNT-polyimide composite films were prepared with a very high degree of CNT dispersion. Specifically, single wall CNT-reinforced polyimide nanocomposites were synthesized by in situ polymerization of monomers of interest in the presence of sonication. This process enabled uniform dispersion of single wall CNT bundles in the polymer matrix. The pre-dispersed CNT solution remained stable throughout the reaction under sonication, producing a reasonably transparent, electrically conductive composites at very low CNT loading.

In this work, double-walled carbon nanotubes (DWNTs) are dispersed in a polyvinylidene fluoride (PVDF) matrix. To the best of our knowledge, there is no study on DWNTs as inclusions in a polymer matrix. DWNTs are a special case of multiwalled carbon nanotubes (MWNTs) that are not sufficiently studied and consequently there is a need to understand their properties. In contrast to MWNTs, where a batch is constituted of tubes with different number of walls, DWNTs have two layers of tubes (see Figure 1) so the effect of the walls can be more precisely analyzed. We will investigate a procedure of dispersing DWNTs in PVDF using no surfactant by taking the advantage of the dipolar concentration in PVDF, and relying on non-covalent interactions between the tubes and the PVDF polymer structure. The effect of adding the DWNTs on the piezoelectricity of PVDF will be assessed. Nanocomposite materials, where the PVDF is the matrix and where the double-walled carbon nanotubes are the inclusions, have suitable applications where electromechancial response is required, such as in sensors and actuators applications.
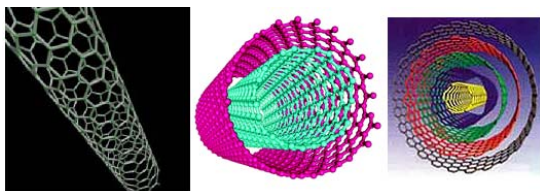

Figure 1. Images of SWNT, DWNT, and MWNT; respectively

NOMENCLATURE

(1) Dual-Walled Carbon Nanotubes (DWNT), (2) Electromechanical Properties (3) Polyvinylidene Fluoride (PVDF).

DWNT-PVDF composites are processed in the presence of a solvent. SEM and TEM images are used to qualitatively probe the dispersion resulting from the processing method. Bulk and surface electrical conductivity techniques are used to investigate the dispersion quantitatively through measuring the percolation threshold concentration for this nanocomposite. The electrical conductivity (σ) was measured as a function of frequency and volume content of DWNT. The dielectric constant (ε) behavior was also studied as a function of frequency and as a function of volume content of DWNT in DC conditions. DSC measurements are done to study the influence of adding DWNT on the melting temperature (T_m), the glass transition temperature (T_g) and the degree of crystallinity of the PVDF matrix. X-ray measurements are done to study the influence of double-walled carbon nanotubes on the piezoelectricity of the PVDF.

Figure 2 shows digital images of PVDF-DWNT solutions in a glass bottle. The digital images show a good stable dispersion of DWNT in PVDF matrix over a period of time. The digital images show that no settling or segregation of the of DWNT-PVDF solution occurs, indicating a good dispersion of DWNTs in the PVDF matrix. This result demonstrates the success of the procedure used for dispersion.

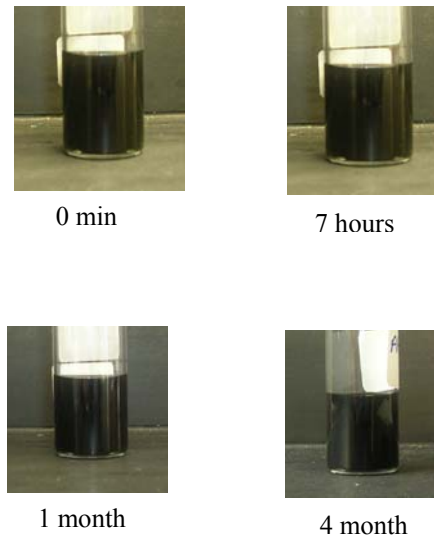0 min   7 hours

1 month   4 month

Figure 2. Digital images of PVDF-DWNT as a function of time.

Figure 3 below shows SEM image of 4.51 vol% DWNT-PVDF sample. Figure 3a shows DWNT in different locations indicating a good dispersion. Figure 3b was used for analyzing

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the dispersion by calculating the diameter of the DWNT bundles in the image. Using Image Tool software to calculate the diameter, an average diameter of 12.19 nm with a standard deviation of ± 2.53 nm is obtained, indicating that small bundles of DWNTs are dispersed in the PVDF matrix.
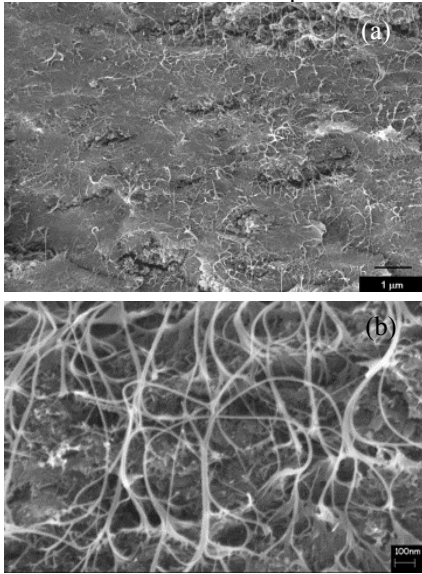

Figure 3. SEM images of 4.51 vol% DWNT-PVDF sample (a) scale bar 1μm (b) scale bar 100 nm.

Figure 4 below shows the conductivity for different weight percent of DWNT as a function of frequency in PVDF matrix. As seen from the graph, there are two different regions. The first region, where the AC conductivity is highly dependent on the frequency, extends from 0 vol% to 0.46vol% DWNT showing an insulator behavior. Below 0.46 vol%, no conduction path in a matrix is formed. Insulator materials are highly dependent on frequency, where conductivity increases with frequency. The second region, where the AC conductivity is independent of frequency, extends from 0.58 vol% up to 4.51 vol%. In this region, a conduction path is formed and the material becomes conductive due to the movement of the charge carriers between the DWNT inclusions.
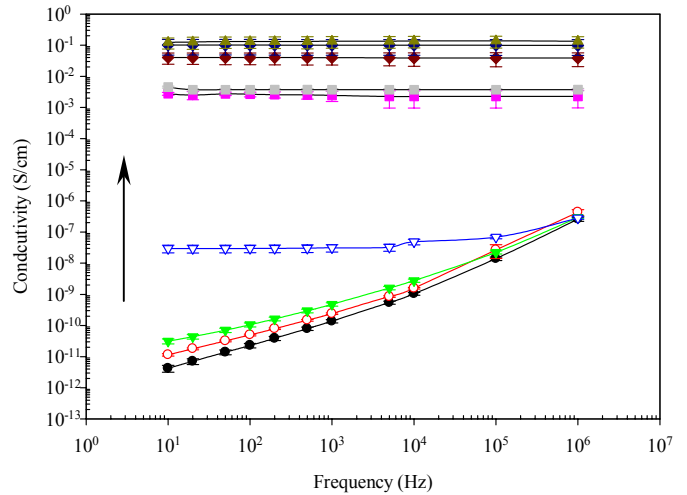

Figure 4. AC Conductivity versus frequency with different vol% of DWNT. Amount of DWNT increases as indicated by the arrow from 0 to 4.5vol%.

To better analyze the insulator-conductor transition, the DC electrical conductivity is plotted as a function of DWNT concentration (Figure 5). A sharp increase is observed between ~0.20 and ~0.40 vol%, where the conductivity changes six orders of magnitude from 1.29×10^{-9} to 3.00×10^{-3}. In addition, a plateau is reached above 0.58 vol% DWNT. The percolation in this nanocomposite occurs between 0.23vol%- 0.46 vol%. In other words, below this concentration the material is very resistant to electrical flow, while at higher concentrations the material is conductive. The dependence of DC conductivity (σ_{DC}) on the DWNTs volume fraction near the percolation threshold [8] is given by a power law relation as shown in Equation 1

$$\begin{cases} \sigma_{DC}(p) \propto (p_c - p)^{-s}, & p < p_c \\ \sigma_{DC}(p) \propto (p_c - p)^{t}, & p > p_c \end{cases} \quad (1)$$

In order to estimate the value of percolation (p_c) and the critical exponent (t) in equation 1, the DC conductivity data has been extrapolated and plotted against the volume fraction of DWNT. These two expressions define two regions; one region below the percolation threshold concentration and the other region above the percolation threshold.
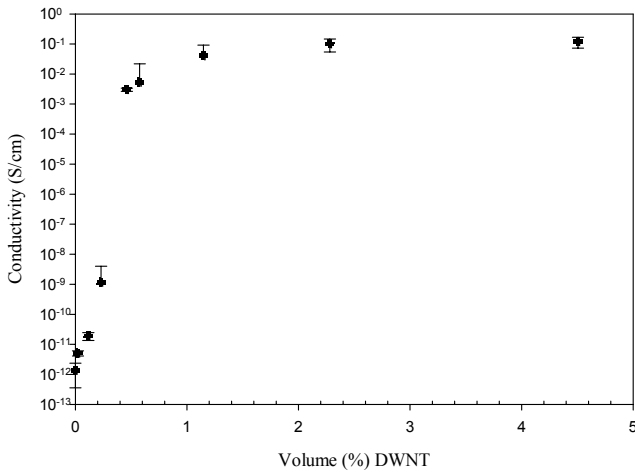
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Figure 5. DC Conductivity as a function of volume (%) of DWNT.

$$\log \sigma = 1.91 * \log(\nu - \nu_c) + 1.34$$
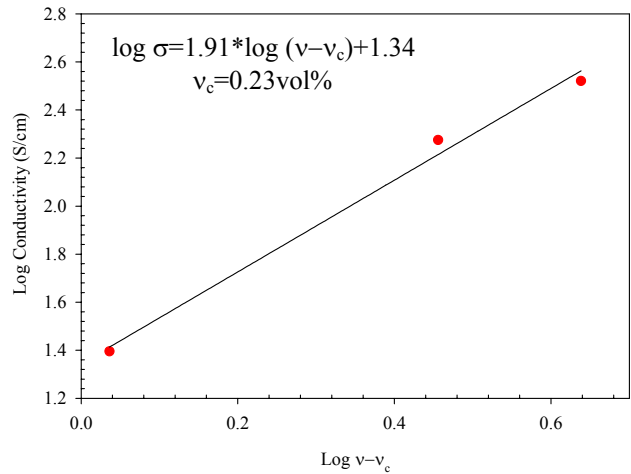$$\nu_c = 0.23 \text{vol}\%$$

Figure 6. Log Conductivity versus log $\nu - \nu_c$

The percolation calculation has been done by noting that percolation occurs in the range from 0.01 to 1.00 at 0.01 intervals. A best fit to the data identifies a percolation threshold value of 0.23vol% (0.19wt%) with 1.91 as the exponent (t) value and an R^2 of 99.19% (Figure 6). Predicted percolation can be calculated assuming the ratio between the radius and the length of the tubes is $(\frac{r}{\ell} << 1)$[9]. The volume fraction at percolation is given in the equation 2 [5]

$$\Phi_c = \frac{\rho_c V_{cyl}}{V_{tot}} \qquad (2)$$

where Φ_c is the volume fraction at percolation, ρ_c is the percolation threshold, V_{cyl} is the volume of the particle which is treated as a capped cylinder, and V_{tot} is the total volume of the sample. The percolation threshold (ρ_c) is inversely proportional to the excluded volume (V_{ex}) which can be calculated as shown in equation 3 [5] in which r and ℓ are the radius and the length of the tube, respectively and Θ is the angle between two tubes which ranged between $\pi/4$ for the isotropic to 0 for aligned samples. In order to be able to assume that ρ_c is inversely proportional to V_{ex} the isotropic case should be assumed.

$$V_{ex} = \frac{32}{3}\pi r^3 + 8\pi \ell r^2 + 4\ell^2 r \sin\Theta \qquad (3)$$

In this work, the double-walled carbon nanotube has a length 2000 nm and diameter of 3 nm. The resulting aspect ratio is of 666.7 and the corresponding $\frac{r}{\ell} = 0.00075$, which is close to zero. The thickness of films used in this work in was ~35 μm, which rescaled to 1. The volume fraction at percolation Φ_c was predicted to be 0.069% after rescaling the radius and the length and recalculate Φ_c using the above equations. 0.069% was calculated by assuming that the bundles consist of one tube.

Recalculating Φ_c by assuming that the bundles consist of 7 tubes forming a hexagonal arrangement, that yields to an aspect ratio of 444.4 and to $\frac{r}{\ell} = 0.0011$, which is still close to zero. The predicted percolation value in this case was 0.20% which is very close to the calculated value 0.23%. This gives an indication that the bundles are arranged in the hexagonal form with 7 double-walled carbon nanotubes grouped together. The diameter of the bundles in this case was 9 nm which is also very close to the calculated diameter from the SEM images in this study which is 12.19±2.53 nm. Recalculating Φ_c by assuming that the bundles consist of 19 tubes, the resultant Φ_c was 0.33%. The experimental results lie between 7 cylinders and 19 cylinders of double-walled carbon nanotubes.

Differential scanning calorimetry (DSC) analysis can be used to indicate degree of crystallinity and specific crystal form present in the PVDF samples under investigation. DSC measurements were completed. Melt temperature (T_m), defined as the temperature at the maximum of the endotherm, recrystallization temperature (T_c), determined from the cool, and heat of fusion (ΔH), defined as the area of the melt peak, are determined and are listed in Table 1.

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Table 1. T_m, T_c, and %Crystallinity for PVDF and PVDF/DWNT Nanocomposite.

DWNT (vol%)	T_m (°C)	T_c (°C)	ΔH (J/g)	%Crystallinity
0.00	158	134.22	52.72	50.69
0.23	160	137.99	52.27	48.33
0.46	162	141.19	47.89	46.04
0.58	160	140.98	47.44	45.62
1.15	164	140.81	44.61	42.89
2.28	160	141.71	39.69	38.16
4.51	160	139.94	34.07	32.76

The trend indicates a decrease in the %crystallinity as DWNT content increases. This indicates that DWNT-polymer chain interaction may interfere with the crystallization of the PVDF. We are currently pursuing isothermal studies, where the temperature is maintained for a few minutes between T_m and T_c to promote crystallization in the presence of DWNTs.

DWNT-PVDF composite films have been prepared by embedding double-walled carbon nanotubes in the polymer matrix. The solution showed a very stable dispersion, even after 6 months. The dispersion is qualitatively confirmed using SEM. Analysis of the SEM images reveals small bundles of 12.19±2.53 nm in diameter. Quantitatively, experimental percolation of 0.23vol% (0.19wt%) is found based on electrical conductivity measurement at DC. This percolation value is very close to the predicted percolation of 0.20%, calculated assuming bundle sizes of hexagonally arranged CNTs (9nm in total size). Effect of DWNTs on the electromechanical behavior and crystallinity of PVDF is ongoing and will be presented in future publications.

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