PEO/PVDF Nanocomposites Preparation with Functionalized Single Walled Carbon Nanotube

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Abstract: System of PEO/PVDF blend with functionalized single walled carbon nanotubes (SWCNTs-COOH) were prepared. The enhanced material properties realized in conventional polymer nanocomposites using different techniques were discussed. The results showed that SWNTs-COOH were covalently linked with the blend through OH and C-C bonds. The intensities of some characteristic vibrational bands for those SWCNTS blends are decreased due to amorphous regions of the prepared samples. The results data are augmented with increases of SWCNTs and the possibility of SWCNTs-COOH to be attached with OH group in the side chain of the polymeric matrices. The interaction between SWCNTs and the blend results in decreasing crystallinity with rich amorphous phase. The amorphous nature is responsible for higher conductivity. The estimated values of the energy gap were increased due to charge transfer complexes. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) illustrated that SWNTs were well dispersed into the polymeric matrix and wrapped with polymer chains. The properties of the blend were enhanced by the presence of SWNTs.

Keywords: polymers; Fourier transform infrared spectroscopy (FTIR); X-ray microscopy; optical properties; electron microscopy.
1. Introduction

Carbon nanotubes (CNTs) are macromolecular of fullerenes ($\text{C}_{60}$). It was discovered by Iijima in 1991 during syntheses of $\text{C}_{60}$ by arc discharge in helium media. It is formed of carbon hexagons rolled into tubes [1, 2]. CNTs are cylinders formed of sheets of graphite capped by fullerene at both ends like structures. There are two kinds of carbon nanotubes, namely, single and multi-walled carbon nanotubes (SWCNTs and MWCNTs) which formed with sheets of graphene rolled about SWCNT. The development of CNT was begun after the production of fullerenes. It has unique properties materials and it is promise materials in the future [2, 3].

The development of research in Physics, Chemistry and material sciences has contributed since of discovery of CNTs. Many properties of CNT are affected by the method of the graphite sheets are rolled. According to the cylindrical structure and the nano scale, CNTs are useful for applications like hydrogen storage. Carbon nanotubes can be produced by different techniques: i) chemical vapor deposition (CVD), laser ablation and arc discharge. Synthesis of CNTs has remains problems not solved especially double walled carbon nanotubes [4-6].

Carbon nanotubes have good electrical and mechanical properties. The properties of CNTs include the characteristics of semiconductor and metal materials due to the high value of optical energy gap which related to the rolling direction and number of the layers of CNTS. Single wall nanotube are 100 times stronger than steel, the thermal conductivity is 5 times that of copper. The density is 1.33-1.41 g/cm$^3$, so, SWCNTs are lighter than aluminum [7].

There three ways to product single and multi-wall carbon nanotubes. In these three methods, gas of methane (CH$_4$) is the main source of carbon that is evaporated separately from a surface of methanol. All techniques are used to fabricate CNTs are vapor deposition (CVD), arc discharge and laser ablation method [8-10].

Polymer nanocomposites are consisted of polymeric materials (e.g., thermoplastics, thermosets, or elastomers). In the simplest method and low cast, adding of nanoparticulates and/or CNTs to a polymer matrix performance of the novel materials with good dispersion of the nanoparticles. The modification of the properties of nanocomposites is due to the ratio and the type of the filler is achieved [11]. The structural, optical, mechanical, electrical, and thermal properties of the novel nanocomposites will different from that of the basic materials [12]. Nanoscale dispersion of the filler in the nanocomposites can introduce best properties, new behaviors and changing of the nature of original polymeric matrices [13].

Methods of fabrication to improve the dispersion CNTs have been focused on to get better properties of nanocomposites. A good dispersion of CNTs in polymeric matrices will be estimate over a
range of diameter scales and can be achieved by characteristic techniques like Raman and optical microscopy, scanning and transmission electron microscopy.

This work reports the synthesis and investigation of PEO/PVDF nanocomposites with functionalized single walled carbon nanotubes (SWNTs-COOH)) using a simple method which achieve a dramatic enhancement in spectroscopic properties.

2. Experiments

2.1. Materials

Polyvinylidene fluoride (PVDF) with MW= 180000 and Polyethylene oxide (PEO) with MW= 900000 were obtained from Sigma Aldrich Company, USA. Purified single wall carbon nanotubes (SWCNTs) with COOH functional groups (NTX10) were obtained from Nanothinx, Greece. CNTs-COOH has diameter 0.8-1.4, length ≥ 5 µm and purity 85%.

2.2. Preparation of Nanocomposites

Both PEO and PVDF were dried at 60 °C in oven to remove their moisture. Appropriate amounts of PEO and PVDF (the ratio between the two polymers is 1:4 wt.%) were dissolved in Dimethyl sulfoxide (DMSO) as a solvent. We get the polymer solution at suitable viscosity.

The obtained solution of the blend was then cooled to room temperature for about 3 hr. SWCNTs-COOH were added separately to 10 ml DMSO in a beaker. The beaker was immersed, to obtain suspension, in the ultrasonic (Eltrosonic type-07) about 40 min. PEO/PVDF nanocomposites containing SWCNTs were prepared using casting method by the following procedure:

Suspension solutions of SWCNTs-COOH was added dropewise to blend solution with continuous stirring and under ultrasonic. The concentration of SWCNTs namely, 0.005 and 0.01 wt.%. A mixing of blend solution with carbon nanotube was dispersed by casting method of PEO/PVDF/SWCNTs nanocomposites films were obtained by peeling off from PET dishes and put it in vacuum oven at 60 °C to evaporation. Prepared samples were kept in a vacuum desiccators before measurement. The thickness of the resulting film was about 20 µm.

2.3. Measurement Techniques

The FT-IR absorption spectra were obtained in the spectral range of 4000–400 cm⁻¹. These spectra were equipped by single beam Fourier transform-infrared spectrometer (FT-IR-430) from JASCO, Japan. The X-Ray diffraction scans were carried out using DIANO corporation-USA with Cu-Kα radiation, λ=1.540 Å and at 30 KV for voltage operation. The ultraviolet-visible spectra were measured at room temperature and wavelength from 190 to1000 nm by spectrophotometer (V-570 UV-
VIS-NIR) from JASCO, Japan. Scanning electron micrographs was obtained from JEOL-JSM 6100 at 30KV operating voltage. Transmission electron microscopy (TEM) images were performed using JEOL-JEM-2010 using a carbon-sputtered sample.

3. Results and Discussion

3.1. Fourier Transform -Infrared Analysis

In this work, FT-IR spectra are used to detect the main bands of PEO and to establish the interaction between PEO/PVDF blend doped with two different contents of SWCNTs. Figure(1a-c) depict IR spectra for PEO, PVDF and PEO/PVDF blend in the range of 4000-400 cm⁻¹. The bands position and the assignments of PEO and PVDF vibrational bands are tabulated in Table 1.

![FT-IR spectra](image_url)

**Figure 1:** FT-IR spectra of: (a) pure PEO, (b) pure PEO and (c) pure blend of PVDF/PEO

As seen in figure 1a, the assignment of the spectra for different phases of PVDF as follows: α-phase with the form TGTG© 482 and the band at 511 cm⁻¹ for CF₂ bending mode, the band at 610 cm⁻¹ for CF₂ bending and skeletal bending modes, at 1073 cm⁻¹ for CH₂ wagging mode and β-phase with the
form TTTGTTTG−; 838 cm−1 for CH out-of-plane deformation and CH2 rocking vibrational modes, 883 cm−1 for CF2 symmetric stretching mode, 1242 cm−1 for CF out-of-plane deformation, 1404 cm−1 for CH2 wagging mode. The vibrational band at 512 cm−1 due to bending vibrations mode of CF2 dipoles, characteristic of TT (trans) conformation of the ferroelectric β-phase [14-16].

**Table 1:** The bands position and the assignments of main characteristic band of PVDF and PEO

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<th>PVDF</th>
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<td>Wavenumber cm−1</td>
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<td>482</td>
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<td>511</td>
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<td>610</td>
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<td>838</td>
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<td>883</td>
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<td>CF2 Stretching mode.</td>
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<td>1242</td>
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<td>CF out of plane.</td>
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<td>1404</td>
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<td>CH2 wagging mode.</td>
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The main characteristic bands of PEO were observed as shown in Figure 1b. A sharp band at 2888 cm−1 is attributed to CH2 stretching of methylene group. The bands at around 1464 cm−1 and 1339 cm−1 were represent CH2 scissoring and CH2 asymmetric bending, respectively. The relatively small band at around 1240 cm−1 is assigned to CH2 symmetric twisting, C-O-C stretching mode has sharp band at 1108 cm−1 out-of-plane rings and C-H bending mode at 962 cm−1[17].

Figure 2 displays absorption spectra of the blend and the blend loaded by 0.005 and 0.01 wt.% of SWCNTs. From the figure, there is a relative reaction between the blend and COOH group in SWCNTs. The intensities of some characteristic vibrational bands for those SWCNTs blends are decreased. This indicates that the amorphous regions of the prepared samples are augmented with increasing SWCNT sand complexation between polymer and filler take place.

The decrease of the bands at 3519 and 2888 cm−1 were observed. These indicate the chemical interactions of SWCNTs with the polymer blend. This change indicates the possibility of SWCNTs-COOH to be attached to O–H group in the side chain of polymer molecules.
Figure 2: FT-IR spectra of pure PVDF/PEO and the blend doped with 0.005 and 0.01 wt.% of SWCNTS

3.2. X-ray Diffraction (XRD)

The X-ray diffraction analysis is very useful to investigate the structure of the polymeric materials and its enable to find out whether a material is crystalline or amorphous. Figure 3(a-c) represented the X-ray spectra of pure PVDF, PEO and PVDF/PEO blend.

Figure 3: X-ray diffraction scans of: (a) pure PVDF, (b) pure PEO and (c) PVDF/PEO blend
The spectra for pure PVDF (figure 3a) of the samples present peaks at $2\theta \approx 23.92$, 42.21 and 46.62°, referent to the diffractions in planes, (1 1 1), (0 4 2) and (1 1 4), respectively, assigned to $\alpha$-crystalline PVDF phase. The peaks at $2\theta = 20.10° (1 1 0)$ and $36.96° (2 0 0)$ are attributed to $\beta$-phase of PVDF. These peaks are disappeared after loading SWCNTs. For PVDF phases, the peaks at $2\theta = 19.09° (020)$ and $39.71° (002)$ for $\alpha$-phase, at $2\theta = 20.01° (110$ or $200)$ and $35.48° (001)$ for $\beta$–phase and at $2\theta = 26.17° (022)$ for $\gamma$–phase are found [18-20]. Two peaks are seen at $2\theta = 18.33°$ and at $23.25°$ assigned to (120) and (112) plans of pure PEO [21]. Since pure PEO have two well defined reflection peaks at $2\theta$ values $19°$ and $23.2°$ as seen in Figure 3b.

Figure 4 represents the X-ray scans of PEO/PVDF blend and the blend with different concentrations of SWCNTS in the range $2\theta = 10$-80°.

![Figure 4: X-ray diffraction scans of PVDF/PEO blend loaded with different concentrations of SWCNTS](image)

On the other hand, all peaks of SWCNTs nano-powder are disappeared in doping samples. This indicates the complete dissolution of the filler in amorphous regions of the polymers. This could be revealed the distortion in crystal structure within polymeric matrices or may be as a result of dilution effect of SWCNTs on the blend matrices which indicates that the complete dissolution of SWCNTs in amorphous regions. A broad of the peaks have been increased in broadness and decreased in intensity suggesting that the amorphicity increases causes as increasing of the conductivity.

It was observed that the reflection of pure blend peaks at $2\theta = 26°$ and $27.1°$ disappeared which revealed that there is distortion in crystal structure of the blend. The tendency of apparently diminution of crystallinity with the increase of SWCNT content in blend sample implies a decrease of the number of hydrogen bonds that are formed between PEO and PVDF if present. The two peaks at $2\theta = 19.1°$ and
23.3° have been found to be increased in broadness and decreased in intensity. The results reveal the increase in amorphous nature of the films.

From all previously mentioned results, the interaction between SWCNTs and polymer blend results in decreasing crystallinity with rich amorphous phase. This amorphous nature is responsible for higher conductivity and confirms the complexation between SWCNTs and the polymer blend.

3.3 Ultraviolet-Visible Spectroscopy (UV-Vis)

Figure 5 displays the UV-Vis absorption spectra in the range of (190-800) nm of PEVDF/PEO films filled with various concentration of SWCNTs content exhibit very small absorbance in the ultraviolet range (200-380 nm) while in visible range showed very high absorbance. Consequently may be used as optically transparent UV absorbing film materials that are easily manufactured by processes that do not utilize volatile organic compounds.

![UV-Vis spectra](image)

**Figure 5:** UV–Vis spectra of PVDF/PEO blend and the blend filled with different concentrations of SWCNTs

The spectrum of pure blend sample exhibited three absorption bands, an intense band at 192 nm ascribed to the presence of groups of PVDF and/or chromophoric groups of PEO, were assigned to the existence of carbonyl groups associated with ethylene unsaturation. A hump or peak at 217 nm and the shoulder at 375 nm may be due to π→π* (K-band) and n→π* (R-band) electronic transitions respectively [22]. In addition, there are no absorption bands on the visible region for all samples since the films are transparent.

Optical absorption analysis is rich by data for band structure of materials. The study of the optical energy for semiconductors is indirect band gap or direct band gap. The transitions from valence band to conduction band should always be associated with a phonon were occur in indirect band gap. The top of
valence band and bottom of conduction band in both laid at the same zero crystal momentum was occurs in direct band gap type. If the bottom of conduction band does not reach to zero crystal momentum then indirect band gap occur. Davis and Shalliday [23] reported that near band edge, both direct and indirect transitions occur and can be calculated by plotting \((\alpha h\nu)^2\) and \((\alpha h\nu)^{1/2}\), respectively, as a function of energy \((h\nu)\), where \(h\) is Planck's constant. The analysis of Thutpalli [24] and Tomlin is based on the following relations:

\[
(\alpha h\nu)^2 = C_1(h\nu - E_{gd}) \quad (1)
\]

\[
(\alpha h\nu)^{1/2} = C_2(h\nu - E_{gi}) \quad (2)
\]

where, \(E_{gd}\) and \(E_{gi}\) are direct and indirect band gap, respectively. \(C_1\) and \(C_2\) are constants and \(\alpha\) is absorption coefficient.

The absorption coefficient \((\alpha)\) can be determined as a function of frequency using the formula [25]:

\[
\alpha(\nu) = \frac{2.303A}{d} \quad (3)
\]

where, \(A\) is the absorbance and \(d\) is thickness of the sample. By plotting \((\alpha h\nu)^{1/2}\) versus photon energy \((h\nu)\) as shown in Figure 6, each linear portion indicates a band energy gap \((E_g)\). The curves are characterized by the presence of an exponentially decay tail at low energy. For indirect electron transitions that require phonon assistance, the absorption coefficient depends on the incident photon energy. Hence the indirect band gap values were obtained from the plots of \((\alpha h\nu)^{1/2}\) Vs. \(h\nu\) at the intercepts of the energy axis on extrapolating the linear portion of the curves to zero absorption value in Figures 6 [26, 27]. The values of the energy gap are decreased 4.94 to 4.91 eV with increasing of SWCNTs content. This indicates that there are charge transfer complexes arose between the polymer blend and SWCNTs.

![Figure 6](image-url): The plot of \((\alpha h\nu)^{1/2}\) versus photon energy \((h\nu)\)
3.4. Scanning Electron Microscopy (SEM)

Surface morphology of the prepared films has been studied by means of scanning electron microscope (SEM). SEM images of the prepared films are presented in Figure 7 (a-e). Micrograph in Figure 7a shows the free surface of pure PVDF/PVDF blend. It is noticed that the micrograph of pure blend was found to be as in previous in literature. After adding SWCNTs, the film surface becomes rough with some small aggregates, but the single rode are well distributed in the entire surface region.

Figure 7: SEM of: (a) pure PVDF/PEO blend and (b–e) PVDF/PEO with different concentrations of SWCNTs at different magnifications
In Figure 7 (a-e), only SWCNTs were observed. When the nanotubes are very short, they are mostly individual and their closed ends can occasionally be resolved. Generally, they often occur either as individual tubes or as thin bundles of a few tubes, which assemble to thicker bundles. Images (a-c) shows a part of a twisted bundle consisting of a few SWCNTs. Generally, the nanotubes appear defect-free with only occasional traces of amorphous carbon deposits on their surface.

3.4. Transmission Electron Microscopy (TEM)

Figure 8(a-f) are the TEM images results of pure SWCNTs. Images (a) and (b) for pure SWCNTs at 200 nm, image (c) at 100 nm and images (e) and (f) at 0.5 µm. Figure 9(a-d) for PVDF/PEO/SWCNTs at 200 nm and 0.5 µm.

![Image of TEM images results of pure SWCNTs at different magnifications](image_url)

**Figure 8:** TEM images results of pure SWCNTs at different magnifications

From figure 8, it can be seen that the SWCNTs was implanted uniformly within the blend and have intimate contact with these polymeric matrices. More ends of broken SWCNTs were observed revealing that the nanotubes broke apart rather than being pulled out from the fracture surface. These indicate the existence of strong interfacial bonding between the CNTs and the blend matrices in the composites. It is also clear that the blend could form a dense covering layer on the images of the composites showing that some defects like ragged and/or worm eaten on the tube walls and walls with
buckles and irreversible bends, which are consequence of the chemical processing. The presence of these defects and the function groups increases the interaction sites along the tubes with the polymeric matrix. Moreover, SWCNTs was arranged in different diameters in the range 8-16 nm and length up to 10 micron and wrapped with polymer blend. This is very useful in technical application. There are some black regions may be attributed to amorphous nature carbon.

![Figure 9: TEM images results of PVDF/PEO blend doped with SWCNTs at different magnifications](image)

**4. Conclusions**

New nanocomposites based on polyvinylidene fluoride (PVDF) and polyethylene oxide (PEO) incorporated with different concentration of SWCNTs were prepared after adding COOH function group to SWCNTs. The structural, optical and morphological properties of the prepared films could be modified by adding SWCNTs. The morphology and performance of these films using scanning electron microscope (SEM) and infrared (FT-IR) was investigated. The structural, optical, and morphological properties were studies by different techniques. Main phases of the blend were observed. The X-ray has revealed decrease in the degree of crystallinity. The film surface by SEM becomes rough with some...
small aggregates and the single rode are well distributed in the entire surface region. SWCNTs was arranged and wrapped with polymer blend. There are some black regions in TEM images attributed to amorphous nature carbon. The prepared nanocomposites are very useful in technical application. There are some black regions may be attributed to amorphous nature carbon.

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References


