

Effect of MWCNT doping on the structural and optical properties of PVC/PVDF polymer blend

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ABSTRACT

Thin film samples of pristine polyvinyl chloride (PVC), poly vinylidene fluoride (PVDF) in combination with their blend in addition to samples containing factorial mass fraction of multi wall carbon nano-tubes (MWCNTs) in the dopant level were prepared via routine casting technique using tetrahydrofuran (THF) as a common solvent. X-ray diffraction and transmission electron microscopy (TEM) depict the nano-scale (15-25 nm) of functionalized MWCNTs with no surface damage results from functionalization process.

X-ray diffraction (XRD) shows a semi-crystalline nature of PVDF with evidence for more than one phase namely α and β phases. The fraction of β phase was calculated and correlated to the dopant content. FTIR optical absorption spectra reveals a preservation of the main vibrational bands before and after addition of MWCNTs in the doping level with a presence of new small band 1151 cm^{-1} assigned for the interaction and complexation between constituents.

Keywords

MWCNTs; PVDF/PVC blend; TEM; FTIR

1- INTRODUCTION

The new era of technology needs for introduction of new materials with superior performance and properties over traditional materials that have been used many years ago. Materials with polymeric backbone constituents was of interest while doping of such materials was recently studied by different authors [1-4].

During last half century much researches devoted for use polymeric materials as replacement of metals and many applications that involve polymeric materials require certain level of electrical conductivity such as electromagnetic radiation shielding, electrodes and electrostatic dissipation. So, addition of electrically conductive dopant to the polymer matrix may enhance their conduction. Carbon nanotubes (CNTs) can be considered as a promising candidate for preparation of an electrically conductive polymeric materials. CNTs exhibit semiconducting to metallic characteristics that depends on their dimensions (length, diameter, specific surface area and surface conductivity) [5-7].

PVDF is a semi-crystalline polymer that contain more than two crystalline forms. β -phase contains trans-planar (TT) chains responsible for piezoelectricity, while α -phase has a random combination of trans-gauche isomers [8]. PVDF has been widely used in biotechnology, biomedical sectors, photo recording and microwave modulation because of its high piezoelectricity, chemical resistance, mechanical strength and process ability [9].

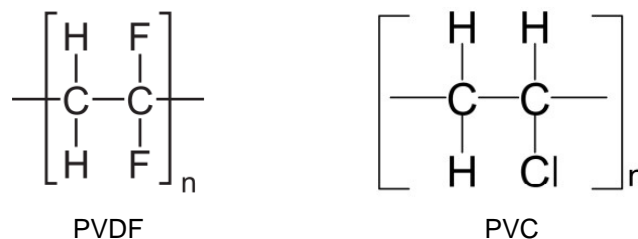
Polyvinyl chloride is a thermoplastic, linear and amorphous polymer with huge commercial and industrial interests due to accessibility to basic raw materials and its superior properties [10].

Present work aims to investigate structural and physical characteristic variations results from blending of two polymeric matrices namely PVDF/PVC in addition to increasing doping level MWCNTs dopant.

2. MATERIALS AND EXPERIMENTAL WORK

2.1. Materials

Multiwall carbon nanotube (MWCNTs) was purchased from Sigma-Aldrich Co., Poly (vinylidene Fluoride) (PVDF Alfa Aesar, A Johnson Matthey company, CAS: 24937-79-9), Powdered poly(vinyl chloride) (PVC High molecular weight) supplied by (Fluka Co.) with molecular weight approximately 100,000 gm/mol (scheme 1) were dissolved in laboratory reagent grade tetrahydrofuran (THF) from (Fisher Chemicals).



Scheme (1) Chemical structure of used virgin polymers

Table 1. Designations and compositions of PVDF-PVC-MWCNTs

Designation	PVDF	PVC	MWCNTs
		(wt.%)	
S00	70	30	0.00
S02	70	30	0.01
S05	70	30	0.02
S10	70	30	0.04
S15	70	30	0.08
S20	70	30	0.10
S30	70	30	0.15

2.1. Methods

Structural investigation was made using Fourier transform infrared (FTIR) absorption spectra in the spectral range of 4000–400 cm^{-1} . FTIR absorption spectra were carried out using the single beam Fourier transform-infrared spectrometer (Nicolet iS10, USA). X-ray diffraction (XRD) scans were obtained using PANalytical X'Pert PRO XRD system using $\text{CuK}\alpha$ radiation (where, $\lambda = 1.540 \text{ \AA}$, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of 5-70°). UV/Vis. absorption spectra were measured in the wavelength region of 200-1100 nm using a spectrophotometer (JASCO V-630 Spectrophotometer, Japan). Transmission Electron Microscopy (TEM) (TEM (JEOL JEM-2100, USA) attached to a CCD camera at an accelerating voltage of 120 kV) was employed to manifest size and morphology of MWCNTs dopant.

3. Results and discussion

3.1. Characterization of MWCNTs

FTIR Spectra of dopant functionalized MWCNTs in the range 4000-400 cm^{-1} recorded using KBr pellet technique (1:100) sample to KBr pressed in the form of transparent disk with a pressure 5 ton/cm^2 in a manual pellet presser. Figure (1) reveals the presence of specified function groups in their positions at about 3440 cm^{-1} associated with O-H stretching groups, 2850 cm^{-1} attributed to asymmetric stretching of CH_2 and at 1650 cm^{-1} results from stretching of (C=O) groups as identified by Misra et al. [6] and Xia et al. [7]. Obtained data suggest the presence of hydroxylic and carboxylic groups on the surface of nanotubes.

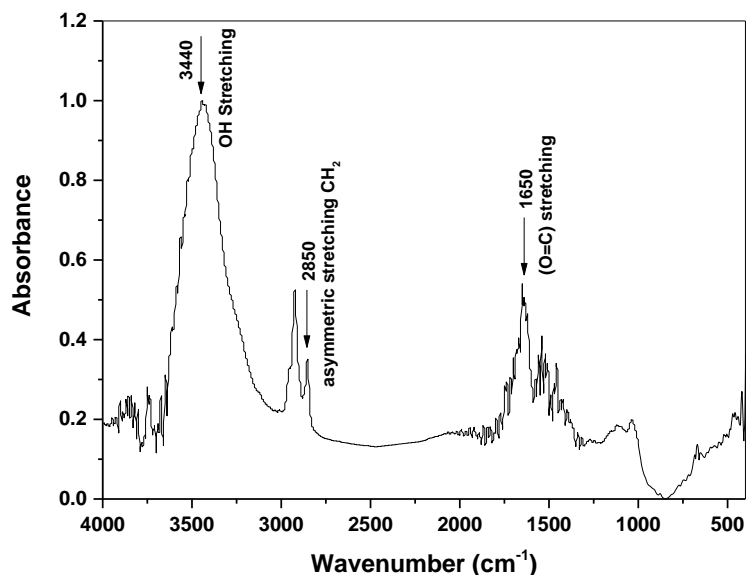


Figure (1) FTIR spectrum of MWCNTs

Figure (2) reveals XRD pattern of MWCNTs dopant combined with TEM image that approve the structure and morphology of nano dopant with radius ranging from 15 to 25 nm. Obtained micrograph depicts no damage results from functionalization process [11].

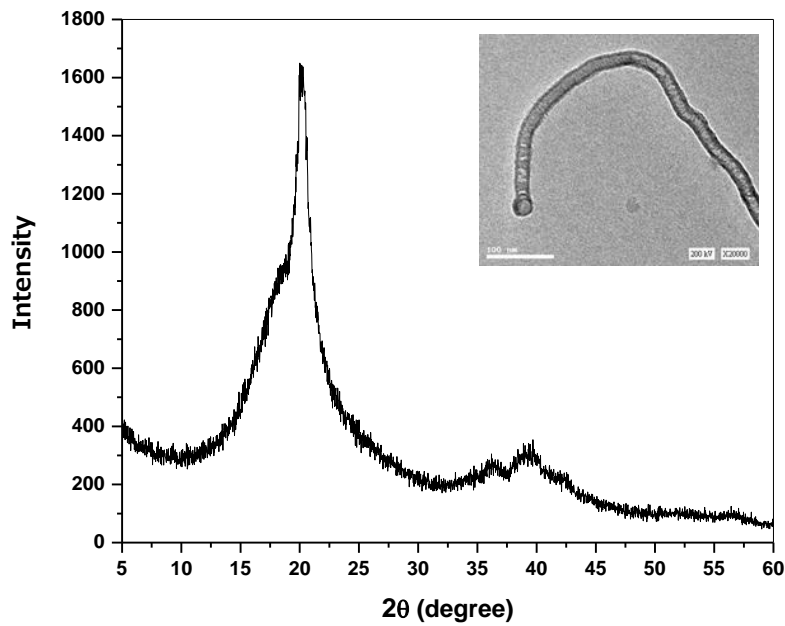


Figure (2) XRD pattern of MWCNTs dopant combined with TEM image

3.2 X-ray diffraction

Figure (3) shows XRD pattern of pristine polymers and their blend films. X-ray patterns of pristine PVC polymer show the amorphous nature and characterize by two halos located at about 18.27 and 24.5° while XRD pattern of PVDF shows a semicrystalline nature with multiple peaks located at 18.30, 26.50, 33.10, 39.10° corresponding to (020), (001), (121) and (002) planes of α -phase and 19.7, 23.5, 36.5° assigned for (200), (210) and (120) planes of β -phase of PVDF. Spectrum of the 70/30 poly blend shows amorphous nature characterized by two halos point out to the complexation and miscibility of the two polymers as indicated by Hartono et al [12].

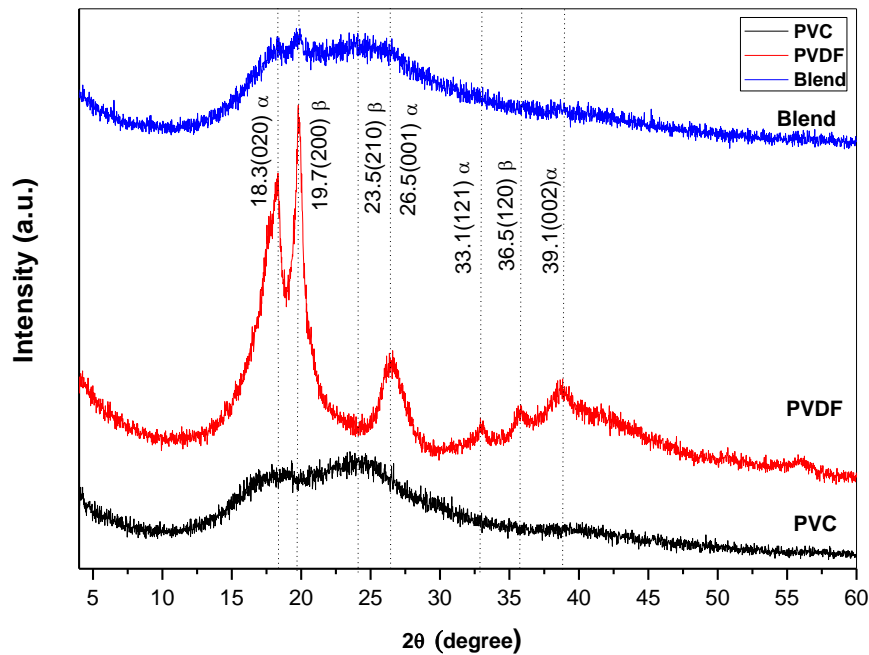


Figure (3) shows XRD pattern of pristine polymers and their blend films.

XRD of poly blend and samples that contains different amount of MWCNTs dopant are shown in Figure (4). XRD pattern shows an increase in the degree of crystallinity results from addition of low level dopant and increase in both crosslinking density and β -phase fraction $F(\beta)$ that calculated according to the following equation;

$$F(\beta) = \frac{A_{\beta}}{1.26 A_{\alpha} + A_{\beta}} \times 100\%$$

Where A_{α} and A_{β} is the sum of relative area corresponding to α and β phases respectively. Disappearance of such characteristic band in the higher ratio (0.15%) of MWCNT may be attributed to complete dispersion of dopant in the polymeric matrices as reported by Allaoui et al. [13].

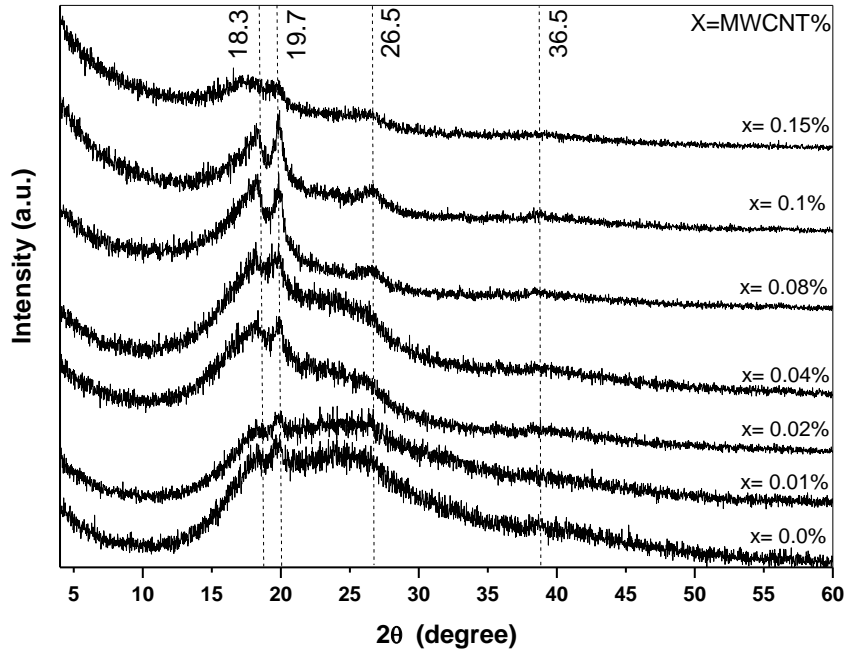


Figure (4) XRD of poly blend and samples that contains different amount of MWCNTs dopant

Calculated values of β -phase fraction was found to obey a polynomial function fit with three degree of freedom and given by;

$$F(\beta) = 4.04 x^2 - 17.4 x + 0.02 ,$$

where x is the weight fraction of MWCNTs. Fitted and calculated data are shown in Figure (5) and listed in table (2).

The change in the general shape of diffraction pattern indicate a homogenous distribution and complete dissolution of the MWCNTs in the polymeric matrix without any evidence for aggregation or phase separation

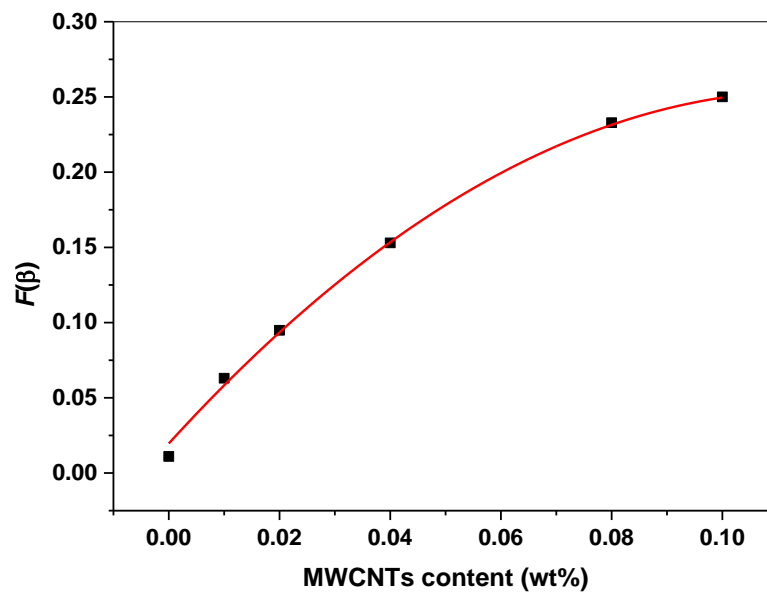


Figure (5) Calculated values of the fraction of β -phase

Table 2 Calculated values of β -phase fraction

MWCNTs Content wt%	F(β) %
0.00	0.0197
0.01	0.0584
0.02	0.0936
0.04	0.1535
0.08	0.2316
0.10	0.2497

3.3. FTIR absorption spectra

FTIR spectroscopy is a powerful nondestructive tool for structural investigation of prepared thin films of virgin and blended polymeric matrices. Figure (6) reveals FTIR absorption spectra of individual polymeric constituent and their blend.

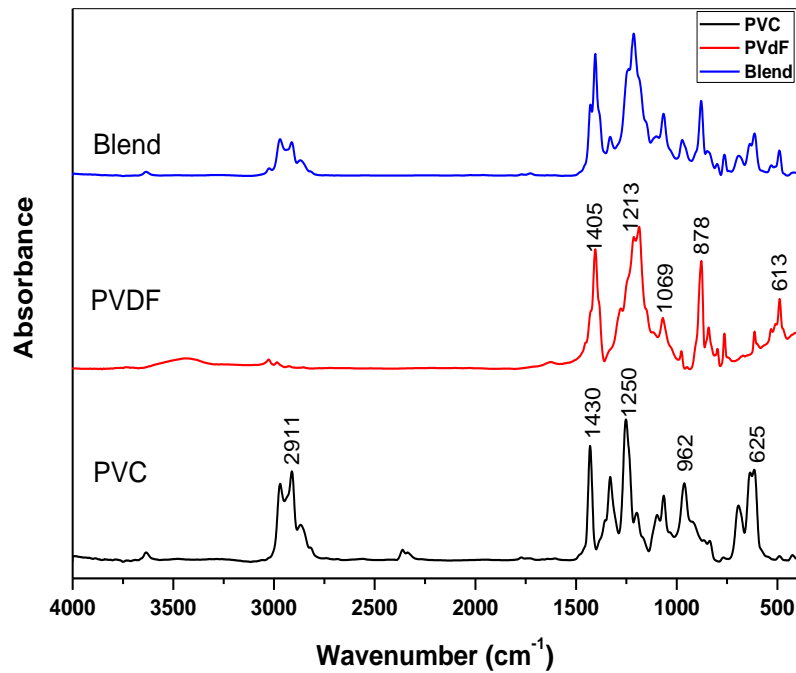


Figure (6) FTIR spectra of pristine polymers and their blend

FTIR spectra of PVC consists mainly of set of peaks in the spectral range 3000-2800 cm^{-1} attributed the C-H stretching vibrations (symmetric stretch at higher wavenumber and asymmetric stretching at lower one) followed by a peak around 1400 cm^{-1} due to aliphatic C-H bonding. The peak at about 1250 cm^{-1} assigned to the bending C-H vibration near Cl, C-C stretching bond vibration of the backbone chain structure located at 1100-1000 cm^{-1} . Finally, the vibration correspond to the C-Cl gauche bond was observed in the range 650-600 cm^{-1} . Spectrum of PVdF includes C-H symmetrical stretching vibration observed in the range 3150 - 3030 cm^{-1} . A series of weak combination and overtone bands appears and the pattern of the overtone bands reflects the substitution pattern of the benzene ring in the spectral range 2000 –1670 cm^{-1} region. α -phase of PVdF is evidenced particularly by the peaks 435, 486, 603 and 768 cm^{-1} , while the β -phase is characterized by the peaks at 510 and 838 cm^{-1} [14]. The peak at 510 cm^{-1} , belonging to the β -phase, are assigned to CF_2 bending and wagging modes. The band at 836 cm^{-1} is assigned to CH_2 bending deformation, belonging to the β -phase [8].

Table (3) list the FTIR band position of constituent pristine polymer and their blend in combination with their assignment previously discussed by different authors [8, 15, 16].

Table 3 FTIR band position and assignment of prepared samples

Sample	Wavenumber (cm ⁻¹)	Assignment
PVC	3000-2800	C-H stretching vibrations
	1400	aliphatic C-H bonding
	1250	bending C-H vibration near Cl
	1100-1000	C-C stretching bond vibration of the backbone chain structure
	650-600	C-Cl gauche bond
PVDF	3150-3030	C-H symmetrical stretching vibration
	2000-1670	weak combination and overtone bands
	435, 486, 603, 768	α-phase characteristic bands
	510, 838	β-phase characteristic bands

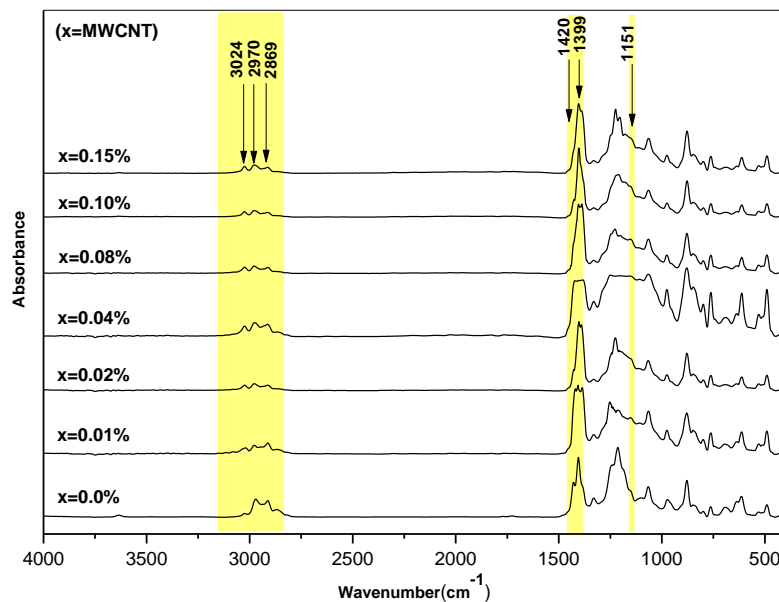


Figure (7) FTIR spectra of poly blend and samples that contains different amount of MWCNTs dopant

Figure (7) depicts FTIR absorption spectra for (PVDF/PVC) poly blend sample and other samples containing variable content of dopant (MWCNTs, 0.01, 0.02, 0.04, 0.08, 0.1, and 0.15 wt. %) that incorporated within the polymeric matrices. The presence of the low intensity broad band at about 1200-1300 cm⁻¹ assigned to the hydrogen bonding between C-H groups from PVC to CF₂ groups of PVdF. In addition, a noticeable change in band intensity and position in comparison of the base poly blend sample were observed especially, for the vibrational bands located at 849, 879 and 1405 cm⁻¹ assigned for the high polarizable γ-phase of PVDF. Mentioned band observed to growth in intensity with increasing content of MWCNTs. A new peak observed at about 1151 cm⁻¹ approve the interaction and complexation process results from addition of MWCNT [17].

Conclusion

Samples of pristine PVC, PVDF and their blend PVDF/PVC (70/30 wt%) in combination with other samples that contain factorial additive masses MWCNTs in the dopant level were prepared via routine casting technique. X-ray diffraction and transmission electron microscopy (TEM) depict the nano-scale (15-25 nm) of functionalized MWCNTs with no surface damage results from functionalization process. While XRD pattern shows amorphous nature of PVC and PVDF/PVC poly blend in contrast to the semi-crystalline nature of PVDF with evidence for more than one phase namely α and β phases. The fraction of β phase was found to increase with quadratic response of dopant concentration. The change in the general shape of diffraction pattern indicate a homogenous distribution and complete dissolution of the MWCNTs in the polymeric matrix without any evidence for aggregation or phase separation. FTIR optical absorption spectra reveals a preservation of the main vibrational bands before and after addition of MWCNTs in the doping level with a presence of new small band 1151 cm⁻¹ assigned for the interaction and complexation between constituents.



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