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THE IMPACT OF f -MWCNT ON PVA/f -MWCNT FILMS PHYSICAL PROPERTIES

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Abstract

Polyvinyl alcohol (PVA) and PVA/functionalized multi-walled carbon nanotube (PVA/f-MWCNT) films were manufactured by a casting method. PVA was dissolved in distilled water, and the doping process of PVA was accomplished by utilizing f-MWCNTs. A different weight ratios (0, 1, 3, and 5 wt%) of the f-MWCNTs were added to PVA for enhance and modify their electrical and optical properties. The FE-SEM images revealed the morphology of PVA and PVA/f-MWCNT films was in generally good diffusion of f-MWCNTs in host polymer. The optical energy gap was determined from optical measurements in the wavelengths in the range of 300–1000 nm. The optical results indicated that the prepared films allowed direct transition, and the optical energy gap was dependent on the weight ratio of f-MWCNT as dopant. The electrical measurements showed that the electrical conductivity of the PVA/f-MWCNT film at 1 wt% was about $7.33E-09$ S/cm, which increased to $92E-08$ S/cm at 5 wt%.

Key words: Polyvinyl alcohol, f-MWCNT, castig method.

1. Introduction

Polyvinyl alcohol (PVA) has several advantages over other polymers such as water solubility, resistance to chemicals, strong dielectric strength, strong mechanical toughness, superior processability, as well as adequate charge storage capacity [1]. In this area, MWCNTs have been extensively utilized to make polymer compounds, but limited advances in mechanical characteristics have been reported. The lack of progress was attributed to various reasons, such as the nanotube dispersion in the polymer, charge difference between polymer particles and nanotubes, structural flaws in nanotubes, as well as nanotube quality [2]. In nanotechnology and scientific and commercial research, carbon-based materials are crucial. Materials containing carbon, like graphene, fullerene (C60), fullerene (C540), amorphous carbon, carbon onions, graphit, and CNTs, have been applied in different essential applications, including drug delivery and luminescent nanomaterials [3]. MWCNTs, which have an electrochemically accessible zone, a large surface area, a high adsorption capacity, aloft electrical conductivity, good chemical stability, and strong mechanical toughness, are drawing growing interest from researchers among carbonaceous materials. [4]. Many applications based on f-MWCNTs have been reported, such as electrochemical sensors, photovoltaics, biomedicine, catalysis, medicine, electronics, and nanocomposites [5,6]. MWCNTs, which have a fiber-like structure, are a carbon nanomaterial with a particular electronic property and different mechanical properties; they are used in extrinsic electrochemical applications [7]. CNTs are known to clump because Van der Waals bonds prevent them from easily disassociating and orienting in the polymer matrix. Therefore, a major goal in the development of high-achievement polymer (CNT) material is to insert CNTs into the polymer matrix to achieve uniformity, enhance strong interactions, and develop charge carriers to the body. Polymer-grafted carbon nanotubes are created by covalently bonding

nanotubes with highly soluble linear polymers like poly(propionylethyleneimine-coethyleneimine) by amide bonds or PVA-co-vinyl alcohol by ester bonds, and the grafted CNTs are soluble in PVA solution films and nanocomposites have good optical properties [8]. The present work aimed to study the morphology, FTIR spectrum, optical properties, and electrical conductivity of PVA films and determine the effect of f-MWCNT doping ratios on the films.

2. Experimental

PVA and PVA/f-MWCNT films were made using the casting process. The host polymeric substance was PVA from BDH with a molecular weight of 107 g/mol, and MWCNTs (Cheap Tube Inc., USA) were used for doping. The functionalization process for MWCNTs was carried out as described in the literature [9]. To prepare PVA solution, To make a PVA solution, 0.2 g of PVA grains were dissolved in 5 ml of distilled water while stirring at 70 °C for 30 minutes.. Doped solution was fabricated by adding different weight ratios (0, 1, 3, and 5 wt%) from f-MWCNT and ultrasonicated in 2 h. After stirring, the solutions were placed into flat glass plate plates and allowed to dry for two days at room temperature. Using a tweezers clamp, the dried homogenous coatings were readily removed. The created films had a thickness of around 25 m, as measured by a digital micrometer. The images of samples by FE-SEM (TESCAN MIRA3 FS- SEM) were studied to determine the spread and distribution of CNTs inside the prepared samples. FTIR (FTIR-8400S, Shimadzu Company) was used to diagnose the functional groups of the samples. Absorbance measurements were taken with a double-beam UV/VIS spectrometer (Shimadzu Japan UV-160A) in the 300–1000 nm wavelength range.

3. Results and Discussion

Figure 1. represents the FESEM images of the prepared PVA and PVA/f-MWCNT films with a magnification of 100× and 200×. All the prepared samples were generally of good homogeneity, and all images showed the homogeneous diffusion of CNTs inside the polymer. Coating these CNTs with the polymeric material led to an increase in the diameters of the CNTs. These images were similar to the irregular network between the CNTs, thereby improving the properties of the mixture. This result was consistent with the findings of S. B. Kndawa, who studied the effect of grafting and CNTs on the properties of polymers [10],[11].

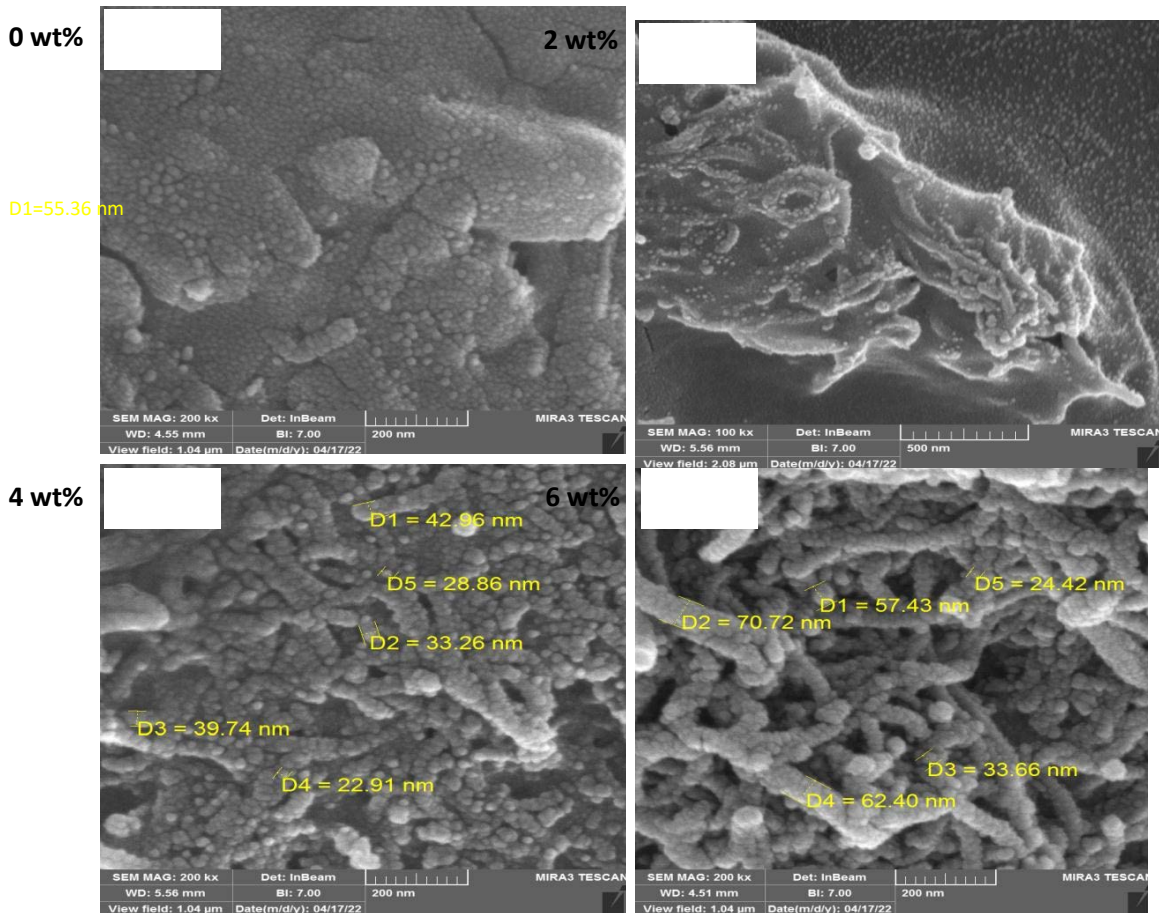


Figure 1: FESEM images for the neat PVA and PVA/f-MWCNT films with different weight ratios.

Figure 2. represents the infrared spectrum of pure PVA films and PVA/f-MWCNT films at the weight ratio of 5 wt%. The characteristic bands of pure PVA films at wavenumbers 2915, 1737, 1639, 1511, 1376, 1014, and 803 cm^{-1} were attributed to CH_2 asymmetric stretching, C=C stretching, C=O stretching, C-H bending, C-H wagging, C-O-C stretching of acetyl groups, and C-H rocking vibrations, respectively [12],[13]. The FTIR spectrum of the PVA/f-MWCNT films revealed an emergence of new peaks due to the presence of f-MWCNT. The peak at 1649 cm^{-1} was related to the C=C stretching vibration of the graphite structure in the MWCNT framework [14]. The peaks at 3448 and 1646 cm^{-1} indicated the presence of strong hydrogen bonds between the -OH groups and also between the -C=O- groups, respectively [15].

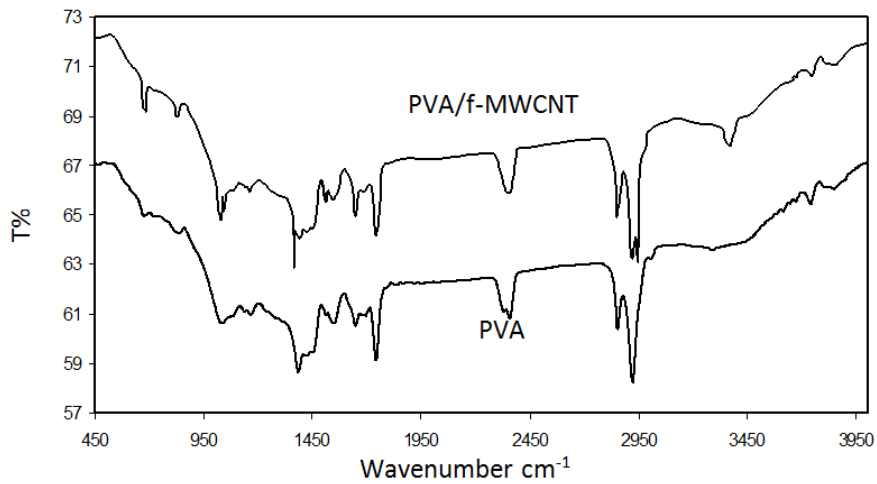


Figure 2. FTIR spectra of PVA and PVA/f-MWCNT films at 5 Wt%.

The voltage–current (IV) characteristic of the PVA and PVA/f-MWCNT films prepared using the casting technique was measured using the two-probe method. The following equation was used to compute DC electrical conductivity [16]:

$$\sigma = \frac{L}{R_a} \tag{1}$$

Where R : resistance, L: length, a the cross-sectional area , of material

The electrical conductivity values are shown in Table (1). In this table, the PVA/f-MWCNT films had the highest conductivity values compared with the PVA films, and it increased as the concentration of f-MWCNTs in the sample increased. This observation was an expected result for the effect of f-MWCNTs on the conductivity when added to polymer matrices, where f-MWCNT networks form in the polymeric matrix, was noticed in the FESEM images, which enhances electrical conductivity. These findings were consistent with the results reported by Tariq and Zain [9] and Kondawar et al. [10].

TABLE 1 Effect of Wt% of f-MWCNT on parameters of the PVA/f-MWCNT films.

SAMPLs	σ S.cm ⁻¹	Eg eV
PVA		3.2
PVA/f-MWCNT : 1Wt%	7.33E-09	2.85
PVA/f-MWCNT : 3Wt%	1.22E-08	2.7
PVA/f-MWCNT : 5Wt%	1.92E-08	2.68

The optical properties of pure PVA and PVA/f-MWCNT films were investigated by using a UV-visible spectrophotometer, and the absorption spectra of films were obtained. Optical characteristics analyzed included the coefficient of absorption α and the optical energy gap E_g in the λ range of 300–1000 nm. The absorption spectra of pure PVA and PVA/f-MWCNT films at different f-MWCNT weight ratios are shown in Figure 3. In general, the absorption of all films decreased with increasing wavelength. By contrast, In the visible and near-infrared ranges, all films displayed good transparency (low absorption). The absorption increased with f-MWCNT weight ratios because of the new excitation energy levels formed by f-MWCNT near the material's band gap [17]. Moreover, the absorption magnitude increased as the weight ratios of the f-MWCNTs increased, and this result was in accordance with what has been documented in the literature [18].

The absorption coefficient was determined using the relationship [19]

$$\alpha=2.303 (A/x) \tag{2}$$

where A , x are the absorption and thickness respectively.

Figure 4. shows that the absorption coefficient decreased as the wavelength of the spectral range of 300–1000 nm increased. The absorption coefficient increased with the increase in the f-MWCNT weight ratios. The value of the α was more than 10^4 cm^{-1} , which indicated that the material had a high probability of direct electronic transitions[19].

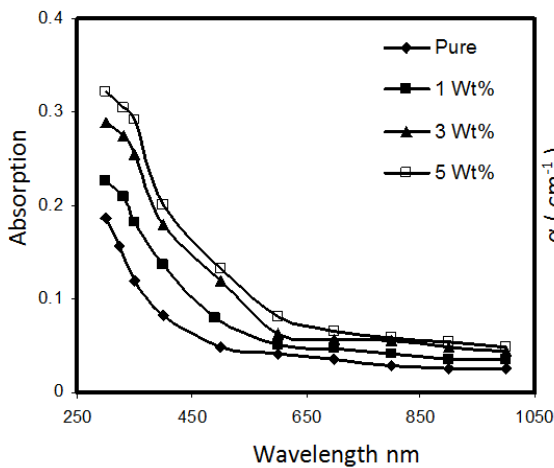


Figure 3: The variation of absorption with wavelength of PVA and PVA/f-MWCNT films

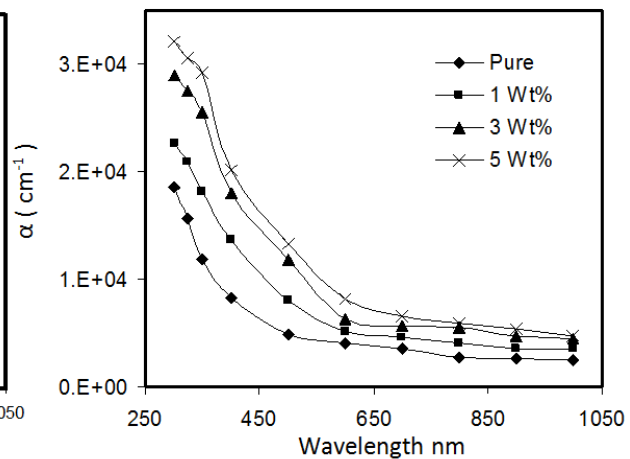


Figure 4: The variation of α with wavelength of PVA and PVA/f-MWCNT films.

The energy gap was calculated in direct transitions according to the relationship [20] :-

$$\alpha hv=A(hv-E_g)^m \tag{3}$$

where, $h\nu$ is the photon energy, E_g is the optical band-gap, B is a constant and m is a constant that can take different values based on the kind of electronic transition, with 1/2 for the direct allowed transfer. For the direct allowed transition, the best fit line is $m= 1/2$. The value of the energy gap, determining the applications of the films used.

The energy gap was calculated by plotting $(\alpha hv)^2$ versus photon energy was dependent on Equation 3. The optical energy gap was determined by extrapolating the portion at $(\alpha hv)^2 =0$ and selecting the best linear component.

Figure 5 and Table 1 show the energy gap values of pure PVA and PVA/f-MWCNT films at different f-MWCNT weight ratios. The energy gap decreased with the increase in the f-MWCNT weight ratios for all samples. This phenomenon occurred due to the modification of the polymer structure as result of the interaction of f-MWCNT with PVA. Moreover, the localized states near the bands increased, lowering the energy gap.

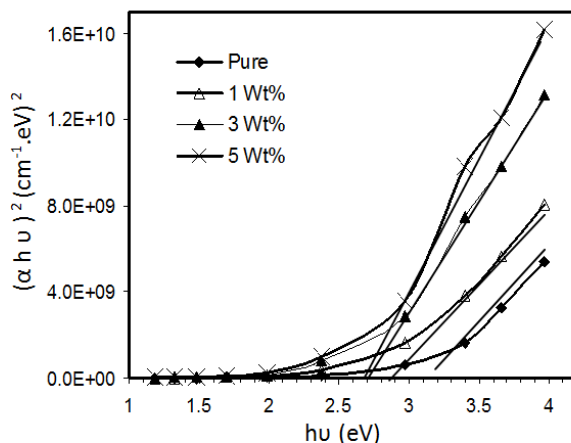


Figure 5 The variation of $(\alpha h \nu)^2$ with photon energy of PVA and PVA/f-MWCNT films.

4. Conclusion

Films with good homogeneity were successfully prepared from pure PVA and PVA/f-MWCNT with different weight ratios of f-MWCNT by the casting method. The process of doping with different weight ratios of f-MWCNT influenced the morphology of PVA and improved the electrical and optical properties of the prepared films in terms of increasing the electrical conductivity and absorption coefficient and decreasing the optical energy gap of the prepared samples.

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