Preparation Of Poly(Vinyl) Alcohol – Multiwalled Carbon Nanotubes Nanocomposite As Conductive And Transparent Film Using Casting Method

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Abstract. PVA nanocomposite was prepared with acid functionalized multiwalled carbon nanotubes as the reinforcing material. The presence of functional groups on MWCNT was revealed by FTIR techniques. Functionalization of MWCNT was conducted by oxidation using acid solution (HNO3 and H2SO4). The functionalized MWCNT induces hydrophilicity to the PVA nanocomposites. Dispersed MWCNT solution was mixed with 10.0% (w/v) PVA as nanocomposite solution (10-40% (v/v)), casted and dried at 60°C. The effect of MWCNT concentration on the electrical conductivities of the PVA nanocomposites was studied very well. The electrical conductivity of the nanocomposites was increased with the concentration of MWCNT, and PVA with 40% (v/v) nanotubes loaded nanocomposite showed better electric properties. Analysis using spectrofotometry UV-VIS show that adding 10% MWCNT has maximum transmittance at 95.52% and minimum transmittance by 40% MWCNT at 38.95%. As the concentration of MWCNT increased to 40% (v/v), the PVA nanocomposites got transformed from a region of insulator to semiconductor was revealed by tauve plot methode. Tensile test was finished to characterizing PVA/MWCNT nanocomposite mechanical properties that show the maximum tensile strength by 40% MWCNT at 45.2 MPa and minimum tensile strength by 10% MWCNT at 36.3 MPa. Change of physical properties describes the existence of important role of MWCNT on the nanocomposite film.

1. Introduction
Polymer nanocomposites are new materials including two or more phases and one of them is in nano-size [1]. The new material obtained was expected to had a new characteristic such in electrical, optical and mechanical properties. All of these properties are needed for applied in transparent conductive film such as optoelectronic device, solar cells, and light emitting diodes.

The first generation of electrodes is based on well established techniques used to make transparent electrodes on glass but with much lower peak processing temperatures. On glass, transparent conducting oxides (TCOs) such as indium tin oxide (ITO), tin oxide, and zinc oxide (ZnO) are sputtered at elevated temperatures (300–600 °C). ITO combines excellent optical transparency (N90%) and low electrical resistivity (~10−4 Ω cm) [2]. Carbon nanotubes (CNTs) have received much attention because of their unique physical properties since their discovery by Iijima in 1991 [3]. Intense research has focused on CNTs composite
materials with enhanced mechanical [4], electrical [5] and thermal properties. Carbon nanotube (CNT) films are emerging as a promising alternative to TCOs, with several advantages. CNT films can be processed from solution at room-temperature, making them suitable for roll-to-roll manufacturing [6]. CNTs are known to have an extremely high Young’s modulus of up to 1 TPa and tensile strength approaching 63 GPa [7]. CNT based transparent films have a comparable cost to ITO based films. CNT based films can also be fabricated to have comparable sheet resistance and transmission to ITO on PET for many applications. Further improvements in CNT materials should continue to increase the DC conductivity of CNT films. Other advantages that CNT films offer over TCOs are reduced reflection (better index matching), more neutral color, resistance to acids, ease of laser patterning, ability to coat rough or curved surfaces, enhanced IR transmission [8]. Results from optical, electrical, and mechanical characterizations of the nanocomposite system are presented and discussed.

2. Experimental

2.1 Materials

The polymer matrix poly(vinyl alcohol) (PVA) which was supplied by Chengdu Alpha Nano tech. Co. Ltd was 95% hydrolyzed. multi-wall carbon nanotubes (MWCNTs) were supplied from Chengdu Alpha Nano Tech. Co. Ltd with 20 nm diameter and length 50 μm. The dispersion of pristine MWCNT in the PVA matrix is very difficult without suitable functionalization. In order to disperse the MWCNT to the PVA matrix, the pristine MWCNT was acid functionalized with H2SO4 and HNO3 [9]. For preparing acid functionalized MWCNT, the pristine MWCNT was treated with 3:1 ratio H2SO4 and HNO3 mixture by sonicating in room temperature. Then the mixture was washed with deionized water up to neutral pH. After attaining the neutral pH, the mixture was filtered and dried in a hot air oven at 60°C.

2.2 Film Preparation

Free-standing PVA composite films with different carbon nanotubes loadings were fabricated. PVA/MWCNT nanocomposites were prepared by solution casting method. In a typical procedure, 10 g PVA was dissolved in 100 mL water using a mechanical stirrer at a temperature of 80°C. Funcionalized MWCNT was added slowly using syringe and stirred for homogeneous solution. Then the homogeneous mixture was casted on dish and dried at 60°C. And then cooled to room temperature. Different set of PVA/MWCNT nanocomposite membranes were prepared by varying the concentration of MWCNT as 0%, 10%, 20%, 30%, 40% (v/v).

2.3 Film Characterization

Fourier Transform Infrared spectroscopy (FT-IR): The presence of multiwalled carbon nanotube particles in the crosslinked nanocomposites were studied by FT-IR analysis. The FTIR spectrum was obtained at a spectrum range of 400–4000 cm⁻¹.

Optical properties: The optical properties of PVA/MWCNT nanocomposites were measured with a UV-VIS Spectrophotometer (Oceanoptic 2000pro). The films were cut and put on the tray of the spectrometer in one mode, transmission spectra was taken from 250 to 1113 nm wavelengths.

Electrical properties: The electrical conductivity of the samples were measured at room temperature by an Hioki 3522 with frequency ranges from 30 Hz to 100 kHz.

Mechanical properties: The mechanical properties (tensile strength and elongation at break) of the films were measured with a Universal Testing Machine (Tensometer LLOYD 2000R). The test specimen were tested according to ASTM D412 for determining the mechanical properties of the composite film using UTM.
3. Result and Discussion

3.1 FT-IR analysis

Introduction of functional groups such as hydroxyl (−OH), carbonyl (−C=O) and carboxyl (−COOH) groups can be obtained by the oxidation of nanotube with a HNO₃/H₂SO₄ mixture [10].

![Figure 1. Schematic representation of side wall functionalisation of nanotubes](image1)

In this research, we obtained the changed of functional groups from 0% MWCNT in PVA nanocomposite with others doped. The presence of functionalized MWCNT in the PVA nanocomposites is clearly obtained from the FT-IR spectra of the nanocomposites (Figure 2).

![Figure 2. FT-IR Spectra of: (a) PVA/MWCNT nanocomposite 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% (v/v)](image2)

The peak around 3200 cm⁻¹ corresponds to hydroxyl (OH) groups, which are always present in the MWCNT samples, and the peak intensity in this region is increased after the chemical treatment. The carbonyl (C=O) stretching peak is obtained around 1714 cm⁻¹ and the peak at 1650 cm⁻¹ corresponds to the carboxylic peak, and the peak intensity increases with chemical treatment [11].

The presence of hydroxyl (OH) functional group each samples 0%, 10%, 20%, 30%, and 40% MWCNT were showed by broad peak around 3271.51 cm⁻¹; 3283.82 cm⁻¹; 3279.38 cm⁻¹; 3276.85 cm⁻¹; and 3273.42 cm⁻¹. The presence of carbonyl (C=O) functional group each samples was showed by stretching vibration at 1732.04 cm⁻¹; 1732.09 cm⁻¹; 1732.15 cm⁻¹; 1732.02 cm⁻¹; 1732.16 cm⁻¹. By the FT-IR spectra showed by the figure 2 knows that the peak intensity increases of carbonyl (C=O) and hydroxyl (OH) functional groups for MWCNT grafting to the carboxylic functional group in PVA was successful. It well-showed by the figure 3.

![Figure 3. PVA grafted by functionalized MWCNT](image3)

3.2 Optical properties

The presence of MWCNT in PVA matrix induced more darkness to the film, decreasing the transparent of nanocomposite. It showed by the figure 4.
Figure 4. Transparency decreasing of: (a) PVA/MWCNT nanocomposite 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40% (v/v)

Figure 5. UV-VIS Transmission spectra

The samples were measured by UV-VIS spectroscopy in transmission mode. Figure 5 showed the decreasing of transmission. In range of UV wavelength (250-450 nm) we obtained that the transmission of each samples were extremely increased, caused a lot of optical absorption by the film. Over the uv wavelength, films just transmit the lights. It’s happened in 450-850 nm wavelength that knows as visible light wavelength.

Table 1. UV-VIS Transmission percentages of nanocomposite

| Sample | $T_{\text{max}}$ (%) | Wavelength at $T_{\text{max}}$ (nm) |
|--------|----------------------|-----------------------------------|
| 10%    | 95.52                | 657.236                           |
| 20%    | 95.88                | 657.236                           |
| 30%    | 95.03                | 1012.63                           |
| 40%    | 38.95                | 1100.417                          |

The transparency of modified MWCNT-PVA nanocomposite decreased with increasing percentage of MWCNT. For the 40% MWCNT loaded, film were absorbed the light, so has the minimal transmission.

Figure 6. $(ahv)^2$ vs $(hv)$ graph of pure PVA
From figure 6 shows that the band gaps of PVA/MWCNT composites were determined from 250 to 1113 nm wavelengths. By *taue plot* method, the band gap of each samples measured. The optical direct band gap was found to be 6.05 eV for pure PVA (Fig. 6). They decreased with increasing MWCNT content. The optical direct band gap was found to be 3.62 eV for 10% MWCNT, 3.56 eV for 20% MWCNT, 3.44 eV for 30% MWCNT, and 1.38 eV for 40% MWCNT containing composite. That means the band gap was decreased by adding MWCNTs.

| Sample | Band Gap (eV) |
|--------|--------------|
| 0%     | 6.05         |
| 10%    | 3.62         |
| 20%    | 3.56         |
| 30%    | 3.44         |
| 40%    | 1.38         |

### 3.3 Electrical properties

The general application of carbon nanotubes is their use as electrically conducting components in polymer composites. However, as shown in Figure 7 the current conduction increased rapidly for the sample containing higher percentages of MWCNT. The conductivity of the neat PVA composite was $4.23 \times 10^{-9}$ S/mm. The maximum current conduction was observed for the sample containing the maximum amount of 40% MWCNT.

### 3.4 Mechanical Properties

Figure 8(a) shows the change in tensile strength with increasing MWCNT content in the PVA/MWCNT nanocomposite films. The tensile strength of the composite films increased with the increase of MWCNT content up to 40% CNT. However, for 30% MWCNT containing PVA nanocomposite tensile strength decreased slightly, down to 41.9 MPa and increased up to 45.2 MPa.
for 40% MWCNT. The agglomeration of MWCNT in nanocomposite might be responsible for this phenomenon so more study while functionalize MWCNT was needed for more desirable performances.

The elongation at break was also increased with adding MWCNT in the pure PVA, as shown in Fig. 8b. The nanocomposites were more stretchy with addition of MWCNT, moreover with 30% MWCNT that has 290% elongation at break.

4. Conclusions
FT-IR, optical transmission, electrical conductivity, tensile strength and elongation at break of PVA/MWCNT nanocomposite with/without MWCNT reinforcement manufactured by simple casting method were analysed. Furthermore, characterizations of nanocomposites was finished for the solution through addition of functionalized MWCNT by 10%, 20%, 30%, and 40% in volume into PVA solution. The optical properties were drastically improved due to MWCNT content in the films. The electrical conductivity increased with increasing MWCNT content in the nanocomposite films. Mechanical properties were also improved with incorporation of CNT. The optical band gap decreased with increasing CNT content.

References
[1] Camaro PHC, Satyanarayana KG and Wypych F. 2009 Mater Res. 12 1
[2] D.C. Paine, H.-Y. Yeom, B. Yaglioglu, in: G.P. Crawford (Ed.).2005. Flexible Flat Panel Displays. John Wiley & Sons, New York 5 79
[3] S. Iijima 1991 Nature 354 56
[4] M. Cadek, J.N. Coleman, V. Barron, K. Hedice and W.J. Blau 2002 Appl. Phys. Lett. 81 5123
[5] B.E. Kilbride, J.N. Coleman, P. Fournet, M. Cadek, A. Drury and W.J. Blau 2002 Appl. Phys. 92 4024
[6] L. Hu, D.S. Hecht and G. Gruner 2004 Nano Lett. 4 2513
[7] O. Lourie and H.D. Wagner 1998 Appl. Phys. Lett. 733527
[8] L. Hu, D.S. Hecht, G. Grüner 2009 Appl. Phys. Lett. 94 81103
[9] Chiang YC, Lin WH and Chang YC 2011 Appl. Surf. Sci. 257 2401
[10] Thomasukutty Jose, Soney C George, Maya MG and Shabu Thomas 2015 Journal of Chemical Engineering & Process Technology 6 1
[11] Moraes FC, Cabral MF, Mascaro LH and Machado SAS 2011 Surf. Sci. 605 435