Synthesis of transparent conductive film containing solution -deposited poly (3, 4-ethylenedioxythiophene) (PEDOT) and water soluble multi-walled carbon nanotubes

Tran Thanh Tung, Won-Jung Kim, Tae Young Kim, Bong Seok Lee, Kwang S. Suh*

Electronics polymer laboratory, Division of Materials science and Engineering, Korea University
5-1, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea

Abstract : The transparent conductive film was prepared by bar coating method of poly (3, 4-ethylenedioxythiophene) (PEDOT) and poly (sodium 4-stylenesulfonate) grafted multi-walled carbon nanotubes (MWNT-PSS) nanocomposites solution on the polyethylene terephthalate (PET) film. In this case, multi-wall carbon nanotubes was treated by chemical methods to obtain water soluble MWNT-PSS and then blending with PEDOT. The non-covalent bonding of polymer to the MWNT surface was confirmed by Fourier transform infrared (FT-IR), thermal gravimetric analysis (TGA) and Transmission electro microscope (TEM) investigation also showed a polymer-wrapped MWNT structure. Furthermore, the electrical, transmission properties of the transparent conductive film were investigated and compared with control samples are raw PEDOT films.
Key words : MWCNT, MWNT-PSS, MWNT-PSS/PEDOT

1. Introduction

Polymer/CNT composite have attracted consider attention because the individual properties of the two components can be combined to give novel hybrid nanomaterials with good unique multifunctional properties, and excellent process ability. However, the main challenges are to improve the dispersion of CNTs in the polymer matrix. In this paper, MWNT was treated to make acylchloride groups (MWNT-COCl), and then a kind of water-soluble anionic polyelectrolyte: poly (sodium 4-styrenesulfonate) was grafted onto the surface of MWNT. MWNT-PSS showed good solubility in water. Finally, it was blending with PEDOT solution which contained 1.3 wt. % of PEDOT powder in DI water to make MWNT-PSS/PEDOT nanocomposite. These solutions were coated onto polyethylene terephthalate (PET) film by bar coating method.

2. Experimental

2.1 Synthesis functional groups of MWNTs

The MWNTs were suspension in acid mixture acids at 80^0C for 4 h, equipped with reflux condenser. The functionalized MWNTs were filtered, washed with a large amount of DI water and vacuum dried at room temperature overnight, obtaining MWNT-COOH. Then the carboxylic acid group will converted into acylchloride groups by the following treatment with $SOCl_2$ and N, N-dimethylformamide (DMF) at 80^0C for 24h then the solvent was removed under vacuum. The remaining solid (MWNTs-COCl) was washed tree times with anhydrous THF and was dried under vacuum at room temperature for 8h.

2.2 Synthesis of MWNT-PSS

0.1 g MWNT as-prepared were added to 10 ml DI water and then kept in an ultrasonic bath for 30 minutes. Then 3 g PSSNa (25% aqueous solution) was added to the suspension. The contents stirred at 100^0C for 24h. After reaction, the PSS-coated MWNT sample was obtained by washed in water, filtration and dried in a vacuum at 35^0C for 48 hours.

2.3 Preparation of nanocomposite

The concentration of 100 mg /l MWNT-PSS in water was kept in an ultrasonic bath for 30 minute.
PEDOT-PSS (1.3 wt% in H_2O) was purchased from Sigma-Aldrich and diluted with DI water (polymer solution to DI water ratio of 5:5) to make solution. The nanocomposite was made by mixing various amounts of MWNT-PSS from 0.05 wt. % to 0.2 wt. % in aqueous solution and polymer stock solution by vigorous stirring for 1 hour. Finally, transparent conductive film were made by coated nanocomposites solutions on the PET film, dried at 80^0C for 5 minutes.

3. Results and discussion

Functional groups of CNT (MWNT-COCl) was attach with polyelectrolyte PSSNa based on electrostatic attraction between oppositely charge species. Follow the Figure 1. in this case, non-covalently absorbed polyelectrolyte PSS anchors on the MWNT-COCl. The physical interaction between hydrophilic PSS chain and surface of MWNT altered the interfacial property of carbon nanotubes. MWNT-PSS samples showed good solubility in water and poor solubility in organic solvents. The soluble brush-like polymer chains pull the relatively huge MWNT backbones into the water phase and help enhance the solubility of carbon nanotubes.

The dispersion behaviors of MWNT-PSS in PEDOT were related with transparency, electrical resistance and flexibility of composite films.

The effect of PSS to functionalize CNTs was evaluated by FTIR and TEM measurements. The properties of composite were checked by TGA, U-V vis and SRC

Fig.2. illustrates the FTIR of MWNT-acid treated and MWNT-PSS. Compare with MWNT, the PSS coated MWNT quite different spectra. The absorption peaks of

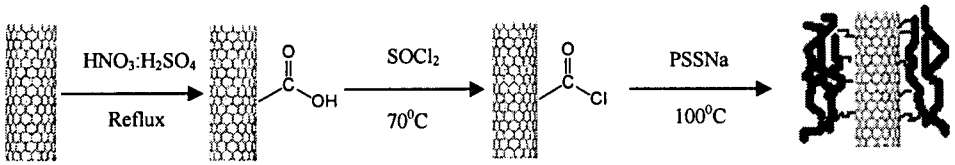

Fig.1. the synthesis of water-soluble multi-walled carbon nanotubes (MWNT-PSS)

the O=S=O stretch appeared at 1152 cm^{-1}, The S-O and C-S stretch appeared at 665 and 644 cm^{-1} respectively.

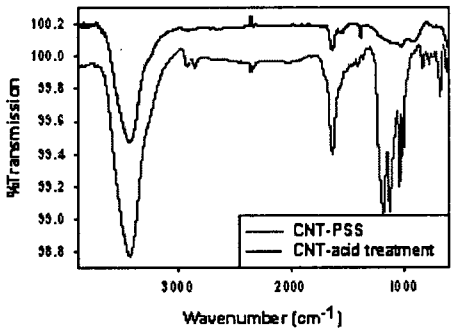

Fig.2. FTIR spectra of MWNT-COOH and MWNT-PSS

TEM image show that, MWNT were covered with a polymer shell. The core-shell structure of polymer-functionalized tube was clearly observed. It made MWNTs dispersion very well in aqueous solution

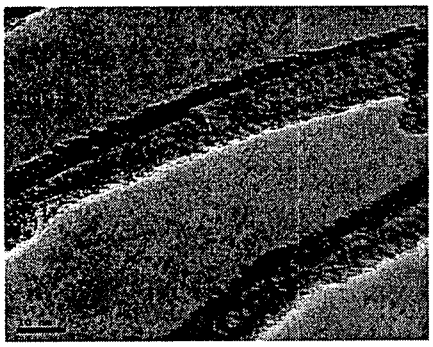

Fig.3. TEM image of MWNT-PSS

The thermal properties of composite were investigated by TGA. Figure 4 shows the TGA data of PEDOT and MWNT-PSS/PEDOT. The PEDOT started to burn around 100°C, however, the MWNT-PSS/PEDOT began to burn around 200°C.

Figure 4 shows the thermal property of composite and compare to PEDOT sample. Fig.5 shows the resistance and transparence of film. It can be seen that increase nanotubes amount from 0.05 wt. % to 0.2 wt. % led to increase conductance and reduces transparence of the film.

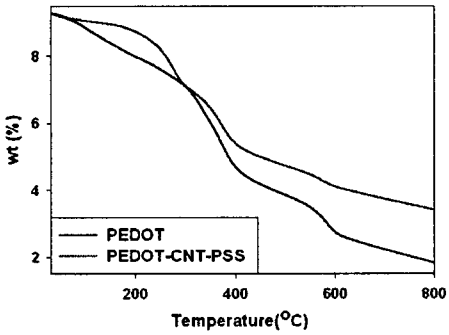

Fig.4. TGA of PEDOT and MWNT-PSS/PEDOT composite

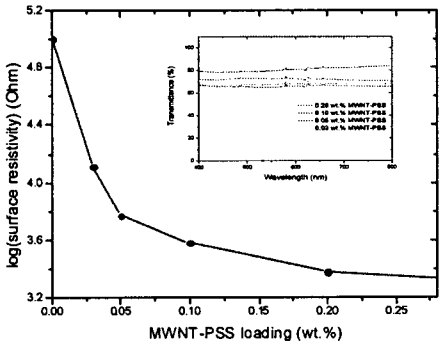

Fig.5. Resistance & transparence follows concentration of MWNT-PSS

4. Conclusions

We investigated that PSS were successfully grafted on the surface of MWNT, resulting in the formation of core-shell nanostructure. More ever, the well dispersion stability of MWNT-PSS in PEDOT solution made increased the conductance of composite.

Reference

[1] A.B. Artyukhin, O. Bakajin, P. Stroeve, A. Noy, Langmuir. Vol. 20, p. 1442, 2004

[2] H. Kong, C. Gao, D. Yan, J. Mater. Chem. Vol. 14, p. 1401, 2004

[3] J. S. Moon et al, Diam. Rela. Mater. Vol. 14, p. 1882, 2005

[4] H. Kong, P. Luo, C. Gao, D. Yan, Polymer. Vol. 46, p. 2472, 2005

[5] Peng Liu, Euro. Pol. J. Vol. 41, p. 2693, 2005