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Fabrication of Anti-Static Carbon Nanotube Film on Polyethylene Naphthalate

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The primary goal of this study was to develop thermally stable, transparent and anti-static films on a flexible polymeric substrate using multi-wall carbon nanotubes (MWCNTs). For this, Polyethylene naphthalate (PEN) was selected as a thermally stable substrate and Poly-methylmethacrylate (PMMA) as a binder between the MWCNTs and PEN substrate. 5 wt% of polymer dispersion agent (PDA) was used to improve the dispersion stability of 1 wt% of MWCNTs in Isopropyl alcohol (IPA). The coating of MWCNT/PMMA was uniformly fabricated on PEN using a bar coater and the prepared films were investigated for their morphology, thermal and opto-electrical properties with applied heat treatment. The MWCNT/PEN films showed superior result according to adhesion test scale (ISO class 0) with excellent heat stability performance at 200°C for 1 h. Furthermore, electrical property of this transparent film was improved through heat treatment. These achieved results highlight the potentiality of this low cost, anti-static CNT films as an attractive material to use in numerous flexible electronic devices.

Keywords Anti-static; conductive film; flexible; heat resistance; MWCNT; PEN; transparent

Introduction

Electrically conductive flexible film electrodes, which are optically transparent to visible light (380–780 nm wavelength range), are essential component for numerous flexible electronic devices like mobile touch screen panels, solar cells, organic light emitting diodes (OLED), e-paper, flexible displays etc. [1–3]. Currently, for transparent conductive coatings indium tin oxide (ITO) is mainly utilized, which is deposited on a substrate by chemical vapour deposition (CVD), sputtering or other methods followed by annealing. ITO glasses have been widely used as transparent

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electrodes due to their excellent conductivity and transparency. However, intrinsic brittleness of ITO layer makes it unsuitable for flexible displays as it losses the conductivity when bents or folds [4,5]. Further, these processes are very expensive and as well, difficult to deal with flexible plastic films [6]. Generally, conducting polymers construct optically clear film with high electrical properties. As a result, transparent polymeric substances are more preferable than glass substrates despite, most of the conducting polymers are heat sensitive when exposed to high temperatures [7,8]. To overcome these problems, an approach to develop and introduce suitable alternatives as transparent and flexible electrodes is highly demanding. In this regard, carbon nanotubes (CNTs) have attracted considerable interest to researchers due to their excellent electrical, physical, chemical, thermal and mechanical properties. Many scientific reports have informed the properties of CNT films about their transparency, conductivity and flexibility [9–17]. The general trend shows, there is an increased demand of Polyethylene terephthalate (PET) substrate for fabricating transparent conducting electrodes than Polyethylene naphthalate (PEN) films. However, PET posses low glass temperature (T_g) than PEN which could exhibit some mechanical problems like thermal shrinkage, dimensional stability, reproducibility in high temperature application for PET [18–21]. Therefore, PEN film was selected in this study as a potential heat stable substrate. PEN films are structurally similar by comparing with the commercially important PET films though there is a competition between PEN and PET films for specific use purposes due to their strength, heat stability and barrier properties. Differences in the physical properties (rigidity) of PET and PEN generally attribute to the larger naphthyl rings in PEN than phenyl rings in PET. Considering all, the present study was aimed to prepare transparent, anti-static PEN films using the one-coating system based on MWCNTs/PMMA.

Experimental

Materials

Multi-walled CNTs were purchased from Acti2O (MWCNT, M90, 10–20 nm diameter, 5–10 μm length, 90% purity). Isopropyl alcohol (IPA) and N-methyl-2-pyrrolidone (NMP) were used as received from Junsei Chemicals Co. (Japan), as solvent and diluents respectively. To obtain the stable MWNT/IPA solution, polymer dispersion agent (PDA, Acrylic block copolymer) was purchased from Ciba (EFKA7700) and was added into the MWNT/IPA dispersion pre-mixture. Poly methylmethacrylate (PMMA, HI-835) was used as a binder to enhance the adhesion between MWNT and Polyethylene naphthalte (PEN) substrate. The PEN films were supplied by SKC Co. (Korea) and were used as a new flexible substrate.

Fabrication of MWCNT/PEN Films

MWCNTs (0.15 g) were suspended in IPA (14.1 g) along with PDA (0.75 g). The PDA has linear C-C main chains with various pendant groups which can interact with the surface of MWCNTs. Therefore the MWCNTs might be dispersed in IPA due to the steric stabilization mechanism by PDA. A homogeneous dispersion of MWCNTs was ensured using a 700 W ultrasound (VC-750, Sonics & Materials

Inc) at 20 kHz of frequency for 1 h. The PMMA binder resin (15 wt%) was separately prepared in NMP. Then the final coating solution of MWCNT/PMMA was prepared by mixing PMMA solution with MWCNT suspension in the ratio of 1:3. At last, transparent conducting layers of MWCNT/PMMA was fabricated on PEN film using a bar coater (No. 6, R. D. S. Webster N.Y). The prepared films were dried at 120°C in a dryer (WOF-155, Daihan) for 1 min.

Measurements

Transmittance and haze performances of MWCNT/PEN films were measured using a UV-vis-NIR spectrometer (V-670, Jasco, Japan) in the range of 380–780 nm. Morphologies of MWCNT/PEN films were characterized using scanning electron microscope (SEM, Hitachi S-2700) images and electrical properties of MWCNT/PEN films were recorded using a four-point probe instrument (K-504RB, Kyowariken Inc, Japan). Adhesion between the MWCNT/PMMA layer and PEN flexible substrate was measured by the standardized crosshatch adhesion test (ISO2409). According to that test, at first several cuts were made on the coated layer using a cutter or hatch and then adhesion tape was attached on the cut areas. After removal of the tape, the grid areas were examined visually. The stability of MWCNT was observed in room condition for at least 1 month. Thermal resistance of the developed films was evaluated by monitoring the changes of surface resistance after heat treatment at 200°C for 1 h.

Results and Discussion

Schematic illustration for the preparation of transparent and flexible multi-walled carbon nanotube conductive films using a bar coater is shown in Figure 1. This method consists of three steps. First, a homogeneous dispersion of MWCNTs as conducting material was obtained by sonochemical process for 1 h with the aid of PDA in IPA. Then, the MWCNT/PMMA coating was prepared by mixing MWCNTs with the binder solution in NMP. As the final step, MWCNT/binder solution was uniformly deposited on PEN substrate followed by drying. PEN was selected here for its heat stability, flexibility and transparency properties. Formation of a homogeneous and well dispersion of coating solution is very important factor for fabricating conducting layer on PEN substrate. Homogeneous dispersion of large amount of CNTs is difficult in a solvent like IPA without addition of dispersion agent due to the formation of agglomerate bundles as CNTs possess high aspect ratio and van der waals forces. To test the long term stability of conducting films, experiment with varying amounts of MWCNTs, PDA along with controllable sonication time was conducted which showed 0.75 g of PDA (5 wt%) with 0.15 g of MWCNT (1 wt%) and 1 hr of sonication developed 1 month stability of prepared films. It was also found that after a month MWCNT coating suspension was still stable and secure to compatible with PMMA. Therefore, development of an optically transparent film using 5 wt% of PDA was in success. Importantly, PDA played a vital role for increasing the storage stability as well, inhibiting the MWCNTs from being agglomerated. As use of lower amount of PDA (range: 1–5 wt%) produced agglomerated coating suspension due to sedimentation of MWCNTS after sonication and which resulted non uniform distribution of conducting layer on PEN (see Fig. 1).

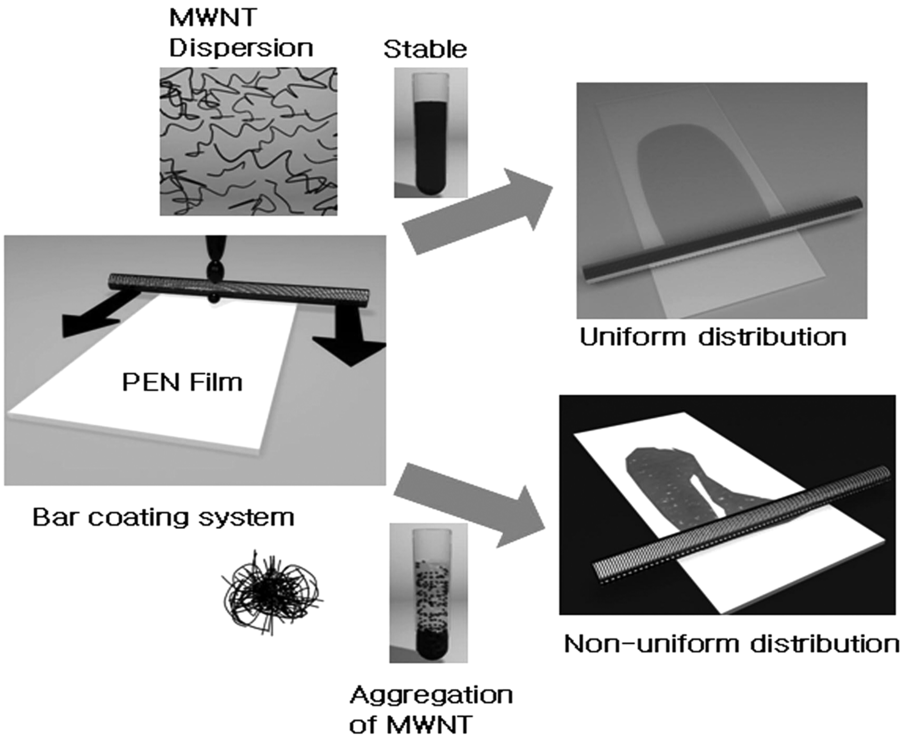

Figure 1. Schematic illustration for the preparation of MWCNT/PEN films using a bar coater.

The SEM images of MWCNT/PEN films are represented in Figure 2 where Figure 2a showed the top view of surface coating image and Figure 2b represented the tilted view of cross sectional image, coating thickness with PEN layer. These images revealed that the MWCNTs were well dispersed into the PMMA binder matrix though showed small surface roughness.

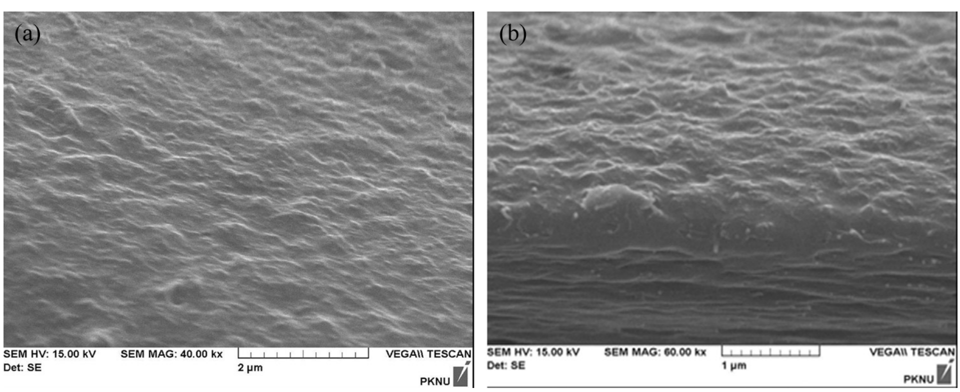

Figure 2. Scanning electron microscope images of the developed MWCNT/PEN films (a) Top view of the coating layer; (b) Tilted view of MWCNT/PEN film.

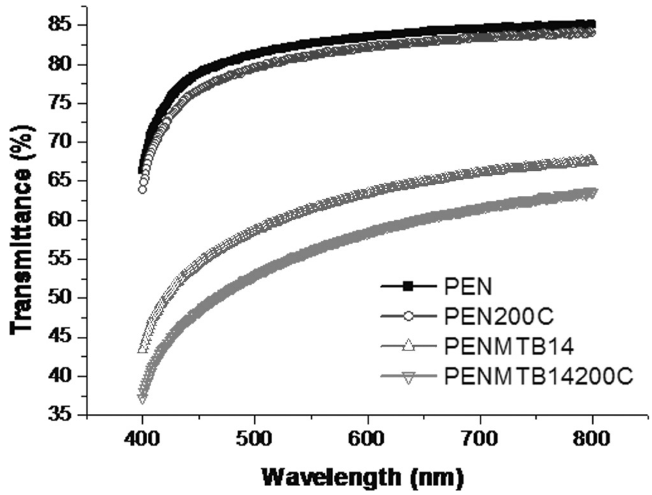

Figure 3. Transmittance (%) of PEN and MWCNT/PEN films before and after heat treatment.

Investigation of adhesion ability of the developed MWCNT/PEN films using the crosscut hatch test (ISO2409) was classified into five ISO scales from 0 to 4, in which 0 represents the superior adhesiveness whereas, 4 denotes poor adhesion. Upon investigation of MWCNT/PEN, it was observed that the film had the result of ISO class 0 (zero), which confirmed that the film had smooth edges and none of squares of the lattice was detached. Indeed, that is an essential character in searching of suitable flexible electrodes for electronic devices.

For examining the opto-electrical performances of MWCNT/PEN films the transmittance (%) data was compared between before and after heat treatment application, represented in Figure 3. The transmittance of both PEN and MWCNT/PEN films found decreased by 1.6% and 5.3% respectively from original values after application of heat treatment at 200°C for 1 hour. Similarly, in case of haze (%) study, both the PEN and MWCNT/PEN films found increased by 9.4% and 12.2% respectively (see Fig. 4 and Table 1). This indicated that the base substrate (PEN) was comparatively thermally more sensitive than the MWCNT/PEN film. This was because, both PEN and coating together effected 12.2% increase of haze which showed approximately 2% change of haze by coating itself. Considering optical point of view MWCNT/PEN conductive layer showed greater heat stability at high temperature. The changing pattern of electrical conductivity was examined at 200°C for 1 h. It showed that with time electrical resistance was gradually decreased from $2.03 \times 10^5\ \Omega/\square$ to $1.51 \times 10^5\ \Omega/\square$ (see Fig. 5), which ultimately proved that electrical conductivity was improved. There could be a possibility of alteration of this electrical conductivity (MWCNT/PEN) by evaporation of residual solvent at high temperature.

The optical microscopic image of a transparent and conductive MWCNT/PEN film has shown in Figure 6. This shows a uniform gray color film that was transparent and flexible.

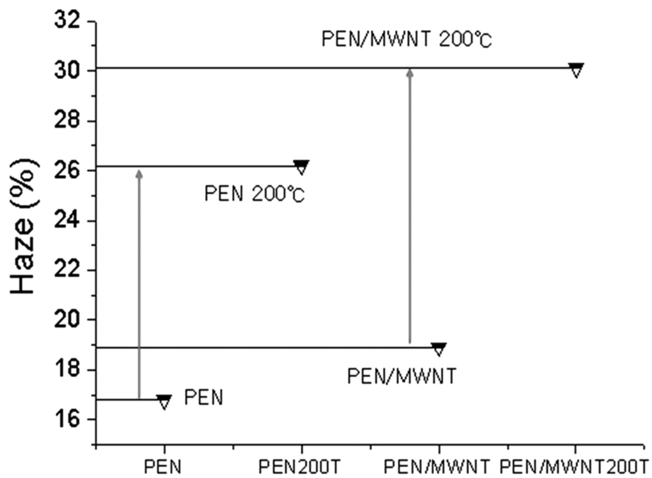

Figure 4. The haze (%) of PEN and MWCNT/PEN films before and after heat treatment.

Table 1. Comparison of opto-electrical properties between PEN and MWCNT/PEN films

	PEN film		MWCNT/PEN composite film	
Properties	Before	After※	Before	After※
Transmittance (%)	82.6	81	61.5	56.2
Haze (%)	16.8	26.2	18.9	30.1
Surface resistance (Ω/□)	–	–	1.95×10^5	1.52×10^5

※Thermal condition: 200°C, 60 min in dry oven.

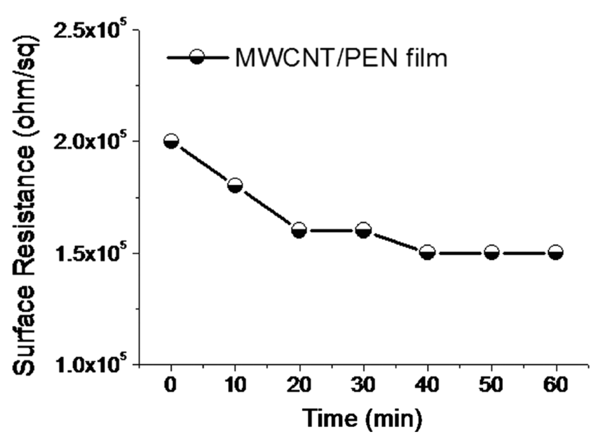

Figure 5. The heat resistance of MWCNT/PEN film during heat treatment.

Figure 6. Optical microscopic image of transparent and flexible MWCNT/PEN film.

Conclusions

In summary, we had successfully developed a transparent, flexible and conductive MWCNT film containing 5 wt% of PDA and 15 wt% PMMA binder. The MWCNTs were well dispersed in PMMA matrix and that improved the adhesion characteristics of the MWCNT/PEN film. The conducting property of the MWCNT/PEN film was also improved with applied heat treatment. As this film could be prepared by a simple process, possible commercial application is expected.

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