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Jin Ho Kim [a b], Jae Mok Jung [a], Chan Park [c] & Kwon Taek Lim [a]

[a] Division of Image Information Engineering, Pukyong National University, Busan, 608-739, Korea

[b] Mapro. co. ltd., 530-11, YongDeok-Ri, HanLim-Myeon, Kimhae, KyungNam, 621-872, Korea

[c] Division of Material Engineering, Pukyong National University, Busan, Korea

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Preparation and Characterization of High Performance Multiwall Carbon Nanotube Conducting Films

JIN HO KIM,[1,2] JAE MOK JUNG,[1] CHAN PARK,[3]
AND KWON TAEK LIM[1,*]

[1]Division of Image Information Engineering, Pukyong National University, Busan 608-739, Korea
[2]Mapro.co.ltd. 530-11, YongDeok-Ri, HanLim-Myeon, Kimhae, KyungNam 621-872, Korea
[3]Division of Material Engineering, Pukyong National University, Busan, Korea

This study was aimed to prepare a high performance multi-walled carbon nanotube (MWCNT) films which could be a heat and solvent resistant conductive film with hardness. MWCNT/ UV resin and poly styrene sulfonate/ poly 3,4-ethylenedioxythiophene (PSS/PEDOT) fabricated on two types of flexible plastic substrates, polyethylene naphthalene (PEN) and polyethylene terephthalate (PET), using a bar coater were also compared each other. MWCNT/UV resin-PEN film exhibited 61% of transmittance, 1.8% of haze, 2.3×10^6 Ω/□ of surface resistance, 2 H of hardness and no shrinkage after the heat treatment.

Keywords MWCNT; Sheet Resistance; Heat Stability; Hardness; PET; PEN; UV-curing; Urethanes

Introduction

Nowadays, carbon nanotubes (CNTs) have been recognized as one of the most reliable candidates for conductive materials due to its remarkable conductivities [1, 2]. Extraordinary electrical, physical, thermal and mechanical properties of CNTs have attracted considerable interest for fabricating CNT hybrid films as advanced materials. Therefore, there is an increasing demand of extensive research to evaluate the potentiality of CNTs in commercially useful microelectronics and optical devices and to provide supporting knowledge regarding the applicability of CNTs [3–6]. Importantly, recent research in this area is targeted to replace glass substrates in a wide range of applications, for instance in touch screens, flat panel displays, optical light emitting diodes, e-paper and solar cells through fabricating the optically transparent and electrically conducting thin polymeric films of CNTs [7–9].

In general, a number of methods are available to prepare nanotube films, for example, vacuum filtration [10], transfer printing onto various substrates [11], spin coating [12],

*Correspondinges author. K. T. Lim, Department of Image Information Engineering, Pukyong National University, Yongdang-dong, Nam-gu, Busan 608-739, Korea (ROK). Tel: (+82)51-629-6409. Fax: (+82)51-629-6408. E-mail: ktlim@pknu.ac.kr

dip-coating [13], direct CVD growth [14], air-spraying [15], and electrophoretic deposition [16] etc. In most of these methods, PET films were used as a flexible substrate, but the poor adhesion of CNTs with the substrates was often problematic [17]. The layer is easily separated from the film because of their sensitivity towards moisture and heat. Therefore, different polymeric binders were proposed to protect the coating of CNTs [18]. The selection of an appropriate polymeric binder and a suitable method of preparation are important factors for maximizing the optoelectronic performance of the films, as the binders optimize interfacial adhesion, abrasion resistance, thermal resistance, transparency, conductivity, and flexibility. Regarding polymeric substrates, there is a competition between polyethylene terephthalate (PET) and polyethylene naphthalene (PEN) based on their specific performances like strength, heat stability and barrier properties. The general trend shows increased market demand for PET in fabricating transparent flexible electrodes compared to PEN. However, PET has lower glass temperature (T_g) than PEN films, which might have some mechanical problems like thermal shrinkage, dimensional instability, reproducibility in high temperature applications.

In this work, multi-walled carbon nanotube (MWCNT) films were compared with conducting polymer PSS/PEDOT films to evaluate its heat resistant. An UV curable coating process was selected for this study as it has recently gained much attention due to the advantages of reaction speed, instant drying, broad formulating range, reduced energy consumption, coating of heat sensitive substrate, and low space and capital requirement for curing equipments [19, 20]. Moreover, bar coating was found to be a simple, fast and cost effective technique to coat the coating materials uniformly and homogeneously on the substrates.

Experimental

Materials

MWCNTs were supplied by Nano-Hub (M90, diameter 10∼20 nm, length 5∼10 μm, purity 90%) for this experiment. 188 μm film of PET (Toyobo, Japan) and 200 μm film of PEN (Teijin, Dupont, Japan) were used as transparent and flexible substrates. Polymer dispersion agent (PDA) was purchased from Ciba. Multifunctional urethane acrylate oligomer (SC-2135, Miwon, Korea), methyl ethyl ketone (MEK, Junsei), a photoinitiator (PI) 1-hydroxy-cyclohexyl-phenyl-ketone (Iracure-184, Ciba) and PSS/PEDOT (Orgacon, Agfa) were used as received.

Fabrication of MWCNT and PSS/PEDOT Coatings on PET and PEN Films Using a Bar Coater

Fabrication of transparent, flexible MWCNT and PSS/PEDOT films on PEN and PET using a bar coater typically consists of three steps. At first, a homogeneous dispersion of MWCNTs in MEK was prepared. For this, 1 wt% of MWCNTs were suspended in MEK (94 wt%) with 5 wt% of PDA and homogenized through ultrasonication (300 W ultrasound VC-750, Sonics & materials Inc. Korea) for 1 h at room temperature. At second step, the prepared MWCNT dispersion was homogenized with multi-functional urethane acrylate oligomer and the photo-initiator. As final step, the MWCNT/UV resin and the purchased PSS/PEDOT conducting polymer were fabricated uniformly as transparent layers on both PET and PEN flexible films using a bar coater (No. 6, R. D. S. Webster N.Y). The MWCNT and PSS/PEDOT films were baked at 90°C for 1 min and at 120°C for 2 min, respectively. A

roll conveyor UV curing instrument (Lichtzen, Model; LZ-U080, Korea) was used for UV curing. The system consists of a metal halide UV lamp with wavelength range of 250∼420 nm and a controller for an adjustable curing speed. For all samples, the amount of exposed UV light was kept constant (total energy density: 500 m J/cm^2).

Characterization

Surface morphology and cross section of the prepared MWCNT/UV and PSS/PEDOT films were analyzed by a scanning electron microscope (SEM-Hitachi S-2400, Japan). Optical properties of the four types of films were compared each other through measuring the transmittance and haze using a UV-Vis NIR spectrometer (Jasco, V-670) in the range of 400∼800 nm. For mechanical properties, pencil hardness test (Elcometer 501) was performed to compare the scratch resistance and hardness of coating films. For electrical properties, a four-point probe instrument (K-504RB, Kyowariken Inc) was used to measure the MWCNT/UV resin films. Transmission electron microscope (TEM) images were obtained on a JEOL (JEM-2010) system. Thermal stability of MWCNT and PSS/PEDOT on PEN and PET films were evaluated by monitoring the changes of electrical resistance and heat shrinkage after heat treatment at 150°C for 90 min followed by 180°C for 60 min.

Results and Discussion

It is well known that a homogeneous and well dispersed coating solution is an important factor for fabricating a conducting and transparent layer on a substrate. To obtain a smooth and flexible conducting layer, experiments were conducted with four different mixing ratios of MWCNTs with the UV curable binder and they were coated on PET and PEN. The MWCNT dispersion was kept constant (5 g) throughout this experiment whereas the weight of the UV oligomer was sequentially increased from 0 to 0.1, 0.5 and 1.0 g with 3 wt% of PI. Surface morphologies of the MWCNT/UV resin and PSS/PEDOT films on PEN investigated by SEM are presented in Fig. 1. These images revealed that MWCNTs were well-entangled into the binder matrix and showed a flat/smooth surface on PEN after UV curing (as well as PET, the images are not shown) when the mixing ratio was 5:0.5 (Fig. 1c). It is also noticeable that the film roughness decreases with an increase in the ratio of the binder content. The film thickness were measured to be in the range from 210 to 400 nm for Fig. 1a, from 320 to 400 nm for 1b, from 500 to 530 nm for 1c, from 460 to 480 nm for 1d, and 100 to 130 for 1e. The best composition of MWCNT/UV resin was found 5:0.5 (10 wt% of the UV resin with respect to MWCNTs), which produced a flexible film with extremely low surface roughness. However, when a large amount of the binder was used (Fig. 1d), the surface layer was cracked. The TEM images of the MWCNT dispersion with and without the UV curable binder are shown in Fig. 2. In the Fig. 2b, MWCNTs were easily seen as a well dispersed form with the binder. Optical performances of the fabricated films on PEN and PET are summarized in Table 1 through transmittance (T) and haze (H) measurements. The T values of the MWCNT films were found to be 61 and 60%, and those of PSS/PEDOT films were 90 and 86% on PET and PEN, respectively. Uncoated PET and PEN films showed no big difference of T (%) either before or after heat treatment (HT). However, HT slightly reduced the T values of PSS/PEDOT coating either on PET or PEN. According to the haze values, uncoated PEN and PET films showed 1.3 and 0.9%, respectively, while HT strongly affected PET films (H 3.8%) compared to the PEN films (H 1.4%). The heat treatment impacted on the H% of all types of fabricated films, and PSS/PEDOT-PET was found to be the most affected type (H 4.3%). Therefore, it can be

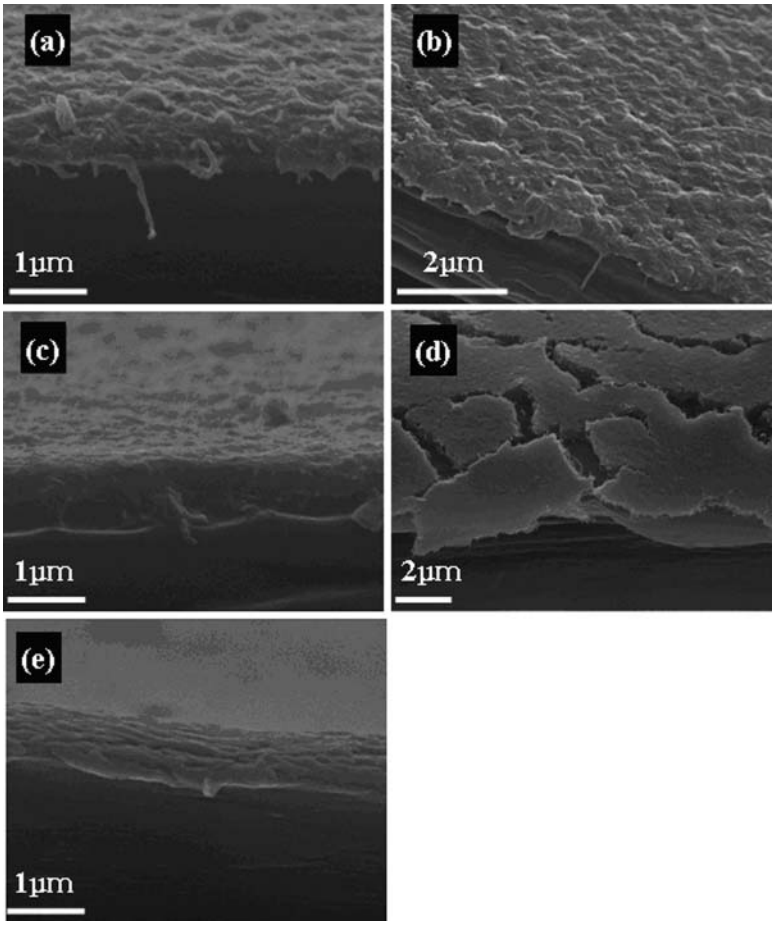

Figure 1. The SEM images of the MWCNT-PEN films with a different ratio of the UV binder, a) 0, b) 2, c) 10, d) 20 wt% of the UV binder, and e) the PSS/PEDOT-PEN film.

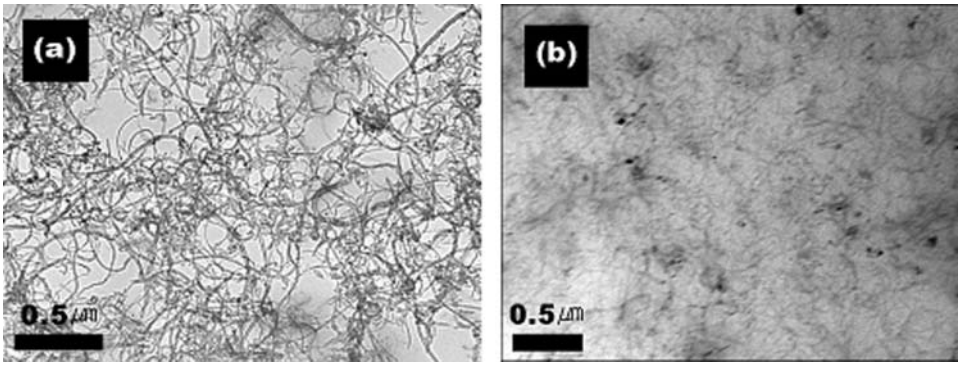

Figure 2. The TEM images of a) MWCNTs and b) the MWCNT dispersion with the UV binder (10 wt% the UV binder).

Table 1. Optoelectrical and mechanical properties of the fabricated films before and after heat treatment.

	PET Film (5 × 5 cm)						PEN Film (5 × 5 cm)					
	PET		PSS/PEDOT		MWCNT		PEN		PSS/PEDOT		MWCNT	
Parameters	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
Transmittance (%)	93	92	90	89	61	61	90	90	86	85	60	61
Haze (%)	0.9	3.8	1.2	4.3	1.6	3.3	1.3	1.4	1.4	1.5	1.6	1.8
Surface Resistance(Ω/□)	–	–	1.1*K*	1.4*K*	22M	2.2*M*	–	–	970	1.3*K*	26M	2.3*M*
Hardness	B	B	HB	HB	2H	2H	B	B	HB	HB	2H	2H
Heat shrinkage (mm)	–	0.1	–	0.1	–	0.1	–	0	–	0	–	0

considered that the fabrication of conducting PET films for high temperature applications is not suitable. Concerning the transmittance and haze values of two conducting layers on PEN, better optical performance of PSS/PEDOT was identified compared to the MWCNT/UV resin.

The electrical surface conductivity of the fabricated films was monitored by measuring surface resistance (SR). I was shown that the SR of MWCNTs/PEN was remarkably reduced after HT. This result may be due to the complete removal of the residual solvent. In contrast, the surface resistance of the PSS/PEDOT layer increased after HT. Based on the electrical performances, the PSS/PEDOT layer was more sensitive to heat than the MWCNT/UV resin film.

From the mechanical performance of the fabricated films, there is no effect of HT on the hardness of the layers. It was also found that the hardness of the MWCNT/UV resin films (2H) was much higher than the PSS/PEDOT films (HB). Irrespective to conductive coating layers, PET films were more sensitive to heat shrinkage (0.1 mm) compared to PEN films (0.0 mm).

Conclusions

The MWCNTs solution with the UV curable binder produced flexible films with low surface roughness due to superior dispersion of MWCNTs in the polyurethane matrix. The surface of the coating layer on the substrate became uniform as an increase in the ratio of the binder content. Any types of the conductive coating layers on PET substrate films seems not worthy for high temperature applications as the film was highly heat sensitive and shrunk after heat treatment. The haze% of PSS/PEDOT-PET found to be highest (4.3%) after HT. Comparing the two types of coating solutions on PEN, marginally better optical performance was obtained from PSS/PEDOT after HT. The surface conductivity of the PSS/PEDOT-PEN films decreased after HT, while it increased after HT in the case of the MWCNT/UV resin films. The hardness of PSS/PEDOT films was comparatively worse than MWCNT/UV resin. Overall, the fabrication of the MWCNT/UV resin on PEN was evaluated as the heat stable conductive transparent film.

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