



The effect of thermal treatment on polymer-dispersed single-walled carbon nanotube transparent conductive film



Taeheon Lee ^{a,1}, Sumin Kim ^{b,1}, Hyunseong Kim ^a, Bong-Soo Kim ^c, Young Sil Lee ^d,
Jong Hun Han ^{e,**}, Hyun-jong Paik ^{a,b,*}

^a Department of Polymer Science and Engineering, Pusan National University, San 30 Jangjeon2-dong, Geumjeong-gu, Busan 609-735, South Korea

^b Department of Advanced Circuit Interconnection, Pusan National University, San 30 Jangjeon2-dong, Geumjeong-gu, Busan 609-735, South Korea

^c Department of Advanced Materials and Applied Chemistry, Kyungnam College of Information and Technology, 45 Jurye-ro Sasang-gu, Busan 617-701, South Korea

^d Kit Convergence Technology Research Institute, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730-701, South Korea

^e Optoelectronics Convergence Research Center, Chonnam National University, 77 Yongbong-roBuk-gu, Gwangju 500-757, South Korea

ARTICLE INFO

Article history:

Received 20 July 2015

Received in revised form

21 October 2015

Accepted 25 October 2015

Available online 10 November 2015

Keywords:

Single-walled carbon nanotube

SWCNT

Thermal treatment

TCF

Conductive film

ABSTRACT

Thermal treatment was performed on polymer-dispersed single-walled carbon nanotube (SWCNT) transparent conductive films (TCFs). By using differential scanning calorimetry, thermogravimetry analysis, Fourier transform infrared and Raman spectroscopies, the proper heating temperature and time were determined, resulting in films with the minimum sheet resistance. The post treatment with proper heating temperature and time was used to decrease the sheet resistance from 1100 to 500 Ω/cm^{-2} with no change in transparency at 250 °C for 1.5 h. The film thickness and surface roughness were reduced significantly, whereas the hardness increased as a result of the more compact film structure. During the heating, the residual polymeric dispersant acquired considerable fluidity causing morphological changes in the SWCNT TCFs. Furthermore, the polymer content on the film was reduced when the thermal treatment was performed above the decomposition temperature of the polymer, as confirmed by the X-ray photoelectron spectroscopy analysis.

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1. Introduction

In recent years, transparent conductive films (TCFs) based on single-walled carbon nanotubes (SWCNTs) have been extensively studied [1–5]. Owing to their intrinsic nanoscale dimensions and electrical properties, they have attracted a lot of attention as a promising alternative to replace indium tin oxide (ITO) electrodes [2,6–8]. To fabricate SWCNT TCFs having excellent electrical conductivity and high optical transparency, it is crucial to efficiently disperse the bundled SWCNTs while retaining the original SWCNT structure as much as possible [9–14]. To exfoliate the bundled SWCNTs, several dispersion methods have been proposed including

covalent functionalization [15,16] and non-covalent functionalization using small molecular surfactant such as sodium dodecyl sulphate, sodium dodecylbenzenesulfonate and Triton X-100 [17,18] or a polymer as a dispersant [19–21]. Among these techniques, non-covalent functionalization using polymeric dispersants is an effective strategy to exfoliate bundled SWCNTs with high aspect ratio while minimizing the structural defect [22–24].

As discussed in our previous report [25], excellent SWCNT dispersed solutions were obtained using poly(((2-dimethylamino) ethyl methacrylate)-co-styrene) (p(DMAEMA-co-St)) as a polymeric dispersant. In addition, transparent SWCNT TCFs with low sheet resistance (R_s) were prepared successfully from it by the spin-coating method. The conductivity of the SWCNT TCFs was, however, lower than expected even though the dispersed SWCNTs on the film had an aspect ratio high enough to satisfy the electrical percolation threshold at a low concentration of SWCNT.

With relation to this phenomenon, we discovered that many aggregates of residual polymeric dispersant on the SWCNT network, as observed by scanning electron microscopy (SEM) [25]. The polymer could obstruct the electrical current in the SWCNT

* Corresponding author. Department of Polymer Science and Engineering, Pusan National University, San 30 Jangjeon2-dong, Geumjeong-gu, Busan 609-735, South Korea.

** Corresponding author.

E-mail addresses: jghan@chonnam.ac.kr (J.H. Han), hpaik@pusan.ac.kr (H.-j. Paik).

¹ These authors contributed equally to this work.

network acting as an insulator. Thus, the presence of residual polymeric dispersant between the SWCNTs might be the primary reason behind the high R_s . Therefore, the polymeric dispersant should be removed in order to have low R_s value which is indispensable in meeting the required surface resistance for the various applications such as touch screen panel. Recently, various approaches have been investigated to enhance the conductivity of SWCNT TCFs through post treatment. Acid treatment with HNO_3 [26] and SOCl_2 [27] have been widely used but the instability of the electrical properties due to the de-doping effect, even under ambient conditions and reported as a serious drawback in many applications [22,28,29].

In this study, we propose a thermal–post treatment as a convenient solution to improve the electrical properties of the SWCNT TCFs. Most of the polymers are less thermally stable than the SWCNTs, so it could be removed by simple heat treatment, resulting in a morphological changes and decomposition of residual polymers. Notably, it has been reported that polymethacrylate could be thermally decomposed at relatively low temperature with cleavage of the ester linkage on the polymer [30]. Park et al. reported that the enhancement of the conductivity of thin film using layer-by-layer (LbL) assembly of SWCNTs by series of post-treatments, involving heating and nitric acid doping [31]. The thermal treatment was performed at various conditions of temperature and time to determine the proper conditions, as confirmed by differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The changes of the morphology of the SWCNT TCFs were observed both by SEM and atomic force microscopy (AFM). Nano-indentation was also conducted to demonstrate the post-heating compact film structure. Furthermore, XPS was used for quantitative elementary analysis.

2. Experimental

2.1. Materials

SWCNTs (1.0–1.2 nm in diameter, 5–20 μm in length) were purchased from NANO SOLUTION Co., Ltd. (Korea) and used as received. 2-dimethylaminoethyl methacrylate (DMAEMA, 98%, Sigma–Aldrich) and styrene (St, 99%, J.T.Baker) were purified before use by passing them through an alumina column to remove the inhibitors. Copper(I) bromide (CuBr , 99%, Sigma–Aldrich) was purified according to a procedure provided in the literature [32]. Tetrahydrofuran (THF, 99.8%, J.T.Baker), 2,2-bipyridyl (bpy, 99%, Sigma–Aldrich), ethyl 2-bromoisobutyrate (EBiB, 99%, Sigma–Aldrich) and methanol (MeOH, SAMCHUN PURE CHEMICALS) were used as received without any further purification.

2.2. Synthesis of polymeric dispersant

The polymer dispersant, $p(\text{DMAEMA-co-St})$, was synthesized by atom transfer radical polymerization (ATRP) as reported in our previous work [25]. A typical polymerization procedure was performed as follows. DMAEMA, styrene, bpy, and anisole were placed in as Schlenk flask under nitrogen atmosphere and five freeze-pump-thaw cycles were carried out to remove the oxygen remaining in the materials. CuBr was added to the flask, and three more freeze-pump-thaw cycles were performed. Then, the initiator EBiB was added to the flask as an initiator for ATRP. The reaction temperature was increased up to 110 $^\circ\text{C}$ under constant stirring and allowed to run at the condition for next 22 h. The Mixture was diluted with THF, passed through a neutral alumina column to remove the copper catalyst, and then isolated into MeOH. The product was finally obtained as a yellow powder after drying under

vacuum at room temperature.

2.3. Dispersion of SWCNTs

Both the synthesised $p(\text{DMAEMA-co-St})$ (30.0 mg) and THF (20.0 mL) were added to a glass vial which was placed in a vortex mixer to dissolve the polymer in the solvent. The SWCNTs (2.0 mg) were added to the solution and dispersed by sonication in a bath-type sonicator for 3 h. The dispersed SWCNT solution was centrifuged (10,000 g for 10 min) to remove any impurities such as the bundled SWCNTs, amorphous carbon and metal catalyst. Subsequently, the dispersed SWCNT solution was obtained by carefully decanting the resulting supernatant.

2.4. Preparation of transparent conductive films

SWCNT TCFs were prepared on a glass substrate using a spin-coating method without any binder. The dispersed SWCNT solution (2.5 mL) was deposited on a glass substrate (20 mm \times 20 mm) at 3000 rpm using a syringe pump with an injection rate of 10 mL/h. The obtained film was rinsed with THF to remove the residual polymer and then dried in a vacuum oven at room temperature.

2.5. Post-thermal treatment

Thermal treatments of SWCNT TCFs were performed under high temperature to understand their effect on R_s . The thermal treatment temperature were conducted on the TCF samples for the temperature range from 100 $^\circ\text{C}$ to 400 $^\circ\text{C}$ with gap of 50 $^\circ\text{C}$ for 1.5 h which treatment time showed the lowset R_s . The furnace was first heated to the set temperature and then the dried samples were placed in the furnace purged with nitrogen gas. After post thermal treatment, the films were kept under vacuum at room temperature overnight and used later for further analysis.

2.6. Characterization

The number average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were determined using a gel permeation chromatograph (GPC) calibrated with polystyrene standards. The GPC was equipped with an Agilent 1100 pump, a refractive index detector (RID) and polymer standard service (PSS) styrenedivinylbenzene (SDV) (5 μm , 10^5 , 10^3 , and 10^2 \AA , 8.0×300.0 mm) columns with THF as the eluent. The synthesized copolymer was characterized using a proton nuclear magnetic resonance (^1H NMR) spectrometer (Varian Unity Inova-500) with deuterated chloroform (CDCl_3) as the solvent. The transmittances and R_s of the TCFs were measured using an OPTIZEN 3220UV UV–vis spectrophotometer (MECASYS Co.) at 550 nm and a CMT-SR1000N 4-point probe measurement (A.I.T.), respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, Q50, TA instrument) was used in order to identify the thermal behaviour of $p(\text{DMAEMA-co-St})$. TGA of the polymer was performed with a Q50 (TA instrument) from 30 to 800 $^\circ\text{C}$ and a heating rate of 10 $^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700 FT-IR spectrophotometer, Thermo scientific) was also used to investigate the effect of thermal treatment on the polymeric dispersant using a NaCl window. X-ray photoelectron spectroscopy (XPS, Theta Probe AR-XPS System, Thermo Fisher Scientific (U.K)) analysis was performed with monochromated Al $K\alpha$ radiation (1486.6 eV) as the excitation source (15 kV, 150 W). The spectrum was corrected based on the C1s peak at 284.6 eV as a reference. Raman scattering spectra of the SWCNT TCFs before and after thermal treatment were measured in backscattering geometry with a JY LabRam HR fitted with a liquid-

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