Table 1 – Bulk density, average pore size and properties of the carbon foams and a comparison with carbon foams reported in

with nanometer pore structure possess much better mechanical and insulation properties than those of conventional carbon foams with micrometer pore structure.

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Highly conductive and transparent thin films fabricated with predominantly semiconducting single-walled carbon nanotubes

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ABSTRACT

A predominantly semiconducting single-walled carbon nanotube-based thin conductive film was fabricated on a flexible poly(ethylene terephthalate) substrate. The structural features of the nanotubes and careful experimental scrutinization consistently yielded the films with very low surface resistance (59 Ω sq⁻¹) and high transparency (80%). The morphological studies of these films before and after acid treatment revealed the self orientation of nanotubes clustered at favorable centers.

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^{0008-6223/\$ -} see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.carbon.2010.03.025 E-mail address: dongwonkim@hanyang.ac.kr (D.-W. Kim).

Advanced research performed over the last two decades has concluded that single-walled carbon nanotubes (SWCNTs) are one of the best substitutes for indium tin oxide in practical applications such as transparent coatings [1–5] and light emitting diodes (LEDs) [6]. In this letter, we report the preparation and characterization of thin conductive films (TCFs) with very low sheet resistance and high optical transparency, which originate from predominantly semiconducting SWCNTs produced by chemical vapor deposition (CVD). The SWCNTs used in this work exhibit high purity, high levels of structural perfection and narrow diameter distribution.

The experimental and fabrication methods were reported elsewhere [4]. The strong adhesion of the nanotube coating over the poly(ethylene terephthalate) (PET) was confirmed by a Scotch tape test [7]. A visible-near infrared (VIS-NIR) spectrum (JASCO V 570) of the SWCNTs/sodium dodecyl sulfate (SDS) dispersion is shown in Fig. 1. The diameter of the nanotubes derived from optical spectra for our bulk nanotube sample as a function of transition in the first semiconducting wavelength region (S_{11}) lies in between 1.04 and 1.14 nm for a particular optical transition occurring at 1365 nm, which is

Fig. 1 – VIS-NIR spectrum of SWCNTs/SDS dispersion.

Fig. 2 – Raman spectrum of the SWCNTs, radial breathing frequency (inset).

Fig. 3 – FESEM images of (a) high purity SWCNTs grown by CVD, (b) TCF on the PET substrate (without acid treatment) and (c) acid treated TCF on the PET substrate.

applicable to nanotube chirality of $(n - m)/3 = 1$. This calculation is based on the model proposed by Bachilo et al. [8] as $\lambda = h c d_t / 2 a_{c-c} \gamma_0$ for tubes that show an optical transition in the S_{11} region. Here, h is Plank's constant, c is the speed of light, d_t is the nanotube diameter, a_{c-c} is the carbon-carbon bond distance, and γ_0 is the interaction energy between neighboring carbon atoms.

The line shape of the non-dispersive graphitic (G) band of the Raman spectrum (Hololab series 5000; excitation wavelength of 785 nm) indicates the semiconducting nature of the nanotubes (Fig. 2). The high purity of SWCNTs was

Fig. 4 – The sheet resistances of different TCFs prepared under identical conditions were plotted as a function of transmittance values. Some of the possible applications (EMI, FPD and TS) and previously reported values of thin films with very low sheet resistance and high optical transmittance are also indicated in the figure.

confirmed by a very low I_D/I_G ratio (0.08). The frequencies of the radial breathing mode (ω_{RBM}) (see inset of Fig. 2) are related to the diameter of the SWCNTs as ω_{RBM} (cm $^{-1})$ = A/d (nm) + B, where A (223 cm^{-1}) and B (10 cm^{-1}) are constants [9]. The diameter of the SWCNT used here was calculated to be between 0.98 and 1.10 nm based on the above equation.

Fig. 3 shows field emission scanning electron microscopy (FESEM-JEOL JSM-6701) images of high purity SWCNTs and TCFs before and after acid treatment. Long carbon nanotubes with spaghetti-like morphologies are observed in Fig. 3a. The long nanotubes with interconnecting networks seemed to be preserved on the PET substrate (Fig. 3b) after spray coating. The acid treated TCF shown in Fig. 3c exhibits an extremely different morphology. A large number of nanotubes are clustered together (size $\sim 0.3 \mu m$; violet double headed arrows) and are separated by distinct channels (blue lines). It is believed that the SWCNTs on PET tend to be denser when treated with nitric acid. However, nanotube densification is difficult to achieve in a TCF as the nanotubes are not in a loose configuration, even though the tendency of tubes to attain dense morphology continues and clusters finally form at favorable centers. This self-orientation of nanotubes creates several well defined channels near the gross-bundles. The long nanotubes/bundles passing via different gross-bundles may also ensure electrical balance between various points all over the substrate.

An optimized TCF offered a sheet resistance of 1050 Ω sq $^{-1}$ in its pristine state with a transmittance of 95%. Nitric acid treatment lowers the sheet resistance of the TCF to 428 Ω sq $^{-1}$ without altering the transmittance. By spraying more of the SWCNT dispersion on the PET substrate, we achieved a very low sheet resistance of 59 Ω sq $^{-1}$ with an optical transmittance of 80% in the acid treated TCF. There are many TCF applications requiring very low sheet resistance and high transparency including electromagnetic induction (EMI) shielding (<80 Ω sq $^{-1}$, 80% T), photovoltaics, LEDs, flat panel displays (FPDs) (<110 Ω sq⁻¹, 80% T), and touch screens (TS) (<500 Ω sq⁻¹, 85% T) [10-12]. For convenience, the electrical and optical requirements for various applications and previously reported values are shown in Fig. 4. It can be seen from the data given in Fig. 4 that the performance of the optimized TCF fabricated by our method is superior to all other TCFs reported in the literature.

In conclusion, the TCF that we fabricated from predominantly semiconducting SWCNTs exhibited very low surface resistance and high optical transparency (59 Ω sq⁻¹, 80% T). These TCFs may be useful in a range of applications such as solar cells, LEDs, EMI shielding, TS, FPD and are expected to be scalable for industrial use.

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Highly conductive polymer composites based on controlled agglomeration of carbon nanotubes

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ABSTRACT

This paper reports an innovative approach to enhance electrical conductivity of fiber composites based on non-conductive fiber and polymer matrix. The dispersion of carbon nanotubes (CNTs) is carried out using a fiber sizing agent which contains uniformly distributed CNTs. The infusion of the sizing agent into the fiber preform prior to resin infusion gives rise to high agglomeration of CNTs on the fiber surface and results in electrical conductivities of 2–3 orders of magnitude higher than those of specimens prepared by a calendering approach.

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Adding a small amount of CNTs can improve the electrical conductivity of fiber-reinforced polymeric composites [1]. It has been shown that CNTs can penetrate into matrix-rich regions among fibers to form an electrically conductive network [2], which has various potential technical applications such as sensing damages in composites [3,4] and in electromagnetic shielding materials [5,6]. One of the major challenges in these applications is the dispersion of CNTs in polymer matrix. Sonication [7], stirring, three-roll mill [8] and other methods have been employed for dispersing CNTs in polymer nanocomposites. However, resin infusion process based on these types of CNT–polymer mixtures are limited by the high viscosity of the CNT–polymer mixtures, which prohibits scaling up of the process to large and thick composites.

In this study, a fiber sizing agent (SIZICYL™ XC R2G, Nano-CYL) was used to improve the electrical conductivity in fiber composite materials. This sizing polymer solution possesses relatively low viscosity and contains well dispersed CNTs. Three groups of specimens were fabricated, namely, three-roll milled CNTs (CVD MWCNTs, Iljin Nanotech)/glass fiber/epoxy (Epon 862, Hexion Specialty Chemicals) composites, glass fiber/sizing agent/epoxy composites and carbon fiber/epoxy composites. For three-roll milled CNTs/glass fiber/epoxy composites, calendering technique was used to disperse 0.5 wt.% CNTs in the epoxy resin. After adding curing agent (Epi-cure, Hexion Specialty Chemicals) to the mixture, the resin was infused into the $[0]_8$ glass fiber preform using conventional vacuum-assisted resin transfer molding (VARTM) at 60 \degree C

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