Chemical Engineering Journal 136 (2008) 409–413

Chemical Engineering Journal

www.elsevier.com/locate/cej

Short communication

Integration of single-walled carbon nanotubes into polymer films by thermo-compression

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Received 12 March 2007; received in revised form 18 April 2007; accepted 21 April 2007

Abstract

We developed a simple and direct thermo-compression method for integrating single-walled carbon nanotube (SWCNT) mats of adjustable thicknesses, transparency and conductivity into polymer films. Produced SWCNT/polyethylene composite films have exhibited good optical transparency and conductivity as well as high mechanical flexibility. It was found that the electrical conductivity of the SWCNT mats could be significantly improved by ethanol densification. SWCNT/polyethylene thin films demonstrated excellent cold electron field emission properties.

Keywords: Carbon nanotube; Conductive; Transparent; Flexible; Polymer; Field emission

Carbon nanotubes (CNTs) and especially single-walled CNTs (SWCNTs) are of great interest due to their unique and useful physical and chemical properties [1,2]. CNT based components have wide ranging applications including light-emitting diodes [3], transistors [4], filters [5], field emitters [6], photovoltaic devices [7] and fuel cells [8]. Ideally, even an individual CNT with a well defined property and in a specific location is sufficient for many applications [9]. However, to date, manipulation of individual CNTs is too difficult, time-consuming and expensive a task to be commercially viable [10–12]. Consequently, for many purposes thin films of CNTs with adjustable physical properties are preferable. Indeed, CNT film based devices have been already successfully used as gas detectors, transparent conductive coatings and field emitters [6,13–15]. Also, they are considered to be strong candidates for ITO replacement in transparent electrodes [14].

An obstacle in the use of CNT mats in industrial applications is in their handling. This is due to, among other factors, their high flexibility and specific surface area, the presence of magnetic catalyst particles and their low density. This leads to stickiness of the mats to surrounding surfaces, e.g., to manipulating instruments and substrates, and to the folding of mats during their treatment which destroys their two-dimensional morphology. Therefore, a simple method to stabilize single-walled CNT mats and to allow them to be incorporated in a variety of applications is desirable. For this purpose, a method to integrate free CNT mats into polymer matrices is useful.

The most direct method for integration of CNTs into polymers is to use the polymer as the growth substrate. This technique is limited, however, due to the high temperatures required for CNT synthesis [16–18]. Therefore, several methods, such as dry printing [19] and electrical or thermal precipita-

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doi:10.1016/j.cej.2007.04.033

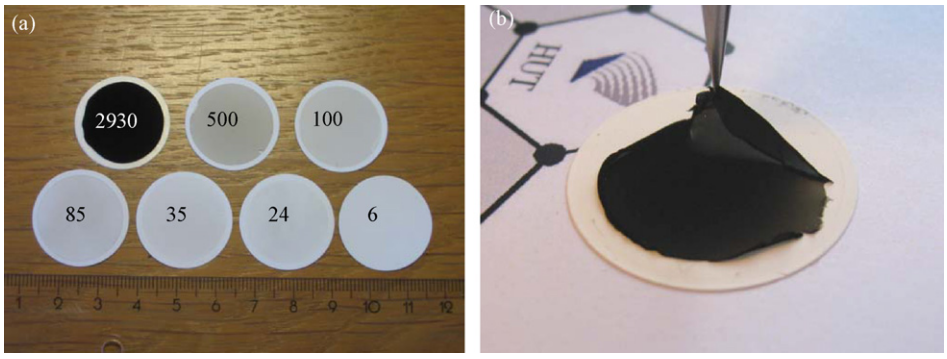

Fig. 1. (a) SWCNT mats collected on nitrocellulose filters (the numbers show the thickness value in nm) and (b) μm thick mats could be easily removed from the filters.

tion [20] have been proposed for transferring nanotubes onto plastics. Nanotubes can also be suspended in solution and sprayed [21] or spin coated onto, e.g., silicon wafers [22], however, such techniques require additional processing steps and equipment.

In this letter, we propose a simple thermo-compression method for easily and efficiently transferring SWCNT mats with adjustable thicknesses, transparency and conductivity into polymer substrates in a single-step process. The usefulness of this method is further demonstrated as a means of producing SWCNT/polyethylene (PE) field emission components.

In this work, SWCNTs were synthesized in a laminar flow aerosol (floating catalyst) reactor using carbon monoxide and ferrocene as a carbon source and a catalyst precursor, respectively [23]. SWCNT mats were then collected directly from the gas phase downstream of the reactor by filtering through 2.45 cm diameter nitrocellulose (or silver) disk filters (Millipore Corp., USA). The deposition temperature on the filter surface was measured to be 45 °C. Depending on the desired mat thickness (Fig. 1a), the deposition time could be varied from a few minutes to several hours. The layer thickness of the collected nanotube mats was measured with a scanning electron microscope (SEM) and an atomic force microscope (AFM). Eight cross sections of CNT mat samples at different mat positions (three in the center and five at the edges) were measured and averaged.

It is worth noting that CNT mats thicker than 1 μm could be easily removed from the filter by simply lifting the mat (as shown in Fig. 1b) and later transferring to a secondary substrate. However, thinner layers tended to be insufficiently robust to remain intact when being similarly removed from the supporting filter and, as a result, could not be easily detached. In this circumstance the thermo-compression method can be used to transfer the mats. In this work, SWCNT mats are transferred to 10 μm thick medium-density PE polymer film (Metsä Tissue Ltd., Finland). This material was chosen because of its suitable physical properties, namely melting temperature ($t_m = 125$ °C) and glass transition temperature ($t_g = -125$ °C) resulting in its good flexibility and optical transparency.

The optimal compression temperature from an optical transparency point of view was experimentally determined by heating films on a hot plate heated to different temperatures. Table 1 shows the transmittance (at a wavelength of 550 nm) of polymer films treated at various temperatures. The optical properties were measured with a Lambda 900 UV/vis/NIR spectrometer (Perkin-Elmer Life and Analytical Sciences, USA) after cooling the polymer film. PE films treated at 100 °C were found to be the most transparent.

For the integration of CNT mats into PE films, the following procedure was performed. The PE film was placed on a heating plate and heated to its thermal treatment temperature at a rate of 5–6 °C/min. Then the filter, coated with a SWCNT mat, was pressed against the heated PE film with a pressure of 0.35 N/cm^2 for 5–10 s. After removing the filter from the PE film, SWCNT mats were found to be successfully transferred. Double sided lamination of SWCNT mats between PE films was also performed as well as laminating several layers of PE films with SWCNT mats in series. Fig. 2 presents transmission electron microscope (TEM) images of the sandwich structure of a 150 nm thick SWCNT mat laminated between PE films. For the TEM observation, a 50 nm thick cross-section of the film was prepared. The dark spots represent catalyst particles in the projection through the 50 nm layer. Low contrast between the CNTs and the PE substrate meant direct TEM observation of the individual tubes at low magnification was difficult, though higher magnification revealed evidence of their orientation. As one can see the mat structure appears uniform and homogeneous. Fig. 2b presents a close-up of the transition region between the PE film and the SWCNT mat, where effective mixing between SWCNTs and PE in the boundary layer, needed for the strong bonding between layers, can be observed.

Since the as deposited CNT mats have low density and, as a result, low contact between tubes (Fig. 3a), prior to the measurements of the electrical properties, the mats of CNTs were

Table 1
Transmittance of cooled PE-MD polymer films used in the thermo-compression technique after different thermal treatments in different temperatures

Thermal treatment temperature (°C)	90	95	100	105	110	115	120	125	130
Transmittance (%)	93.5	94.0	96.0	95.5	95.0	93.0	93.0	90.0	60.0

Table 2
Effect of densifying SWCNT mats of different thicknesses with ethanol as measured by SEM (≥85 nm) and AFM (≤50 nm)

Layer thickness before ethanol (nm)	24	35	50	85	100	1000	2930
Layer thickness after ethanol (nm)	21	29	44	75	87	850	2600
Mat thickness decrease (%)	13	17	12	12	13	15	11

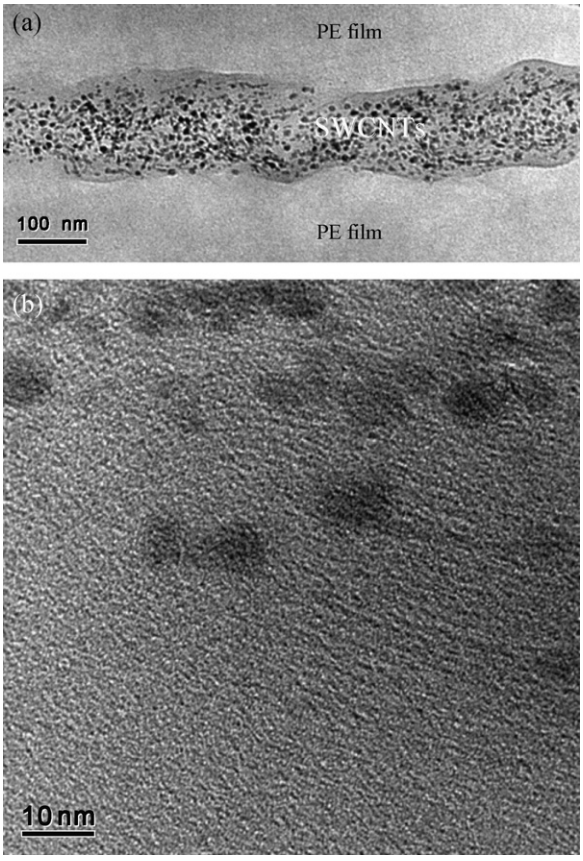

Fig. 2. (a and b) TEM images of a sandwich PE/SWCNT/PE structure.

compacted by adding a droplet of ethanol to the transferred layer (Fig. 3b). Table 2 presents the increased densities (decreased layer thicknesses) of the studied nanotube mats as measured with SEM and AFM. In general, the densification of the SWCNT mats led to a change in thickness of approximately 13%, while the square resistance was found to decrease more significantly. For the electrical conductivity measurements, SWCNT mat samples of 1 mm wideness were placed on top of two copper electrodes with a gap between of 1 mm. An ethanol droplet added to the sample initially resulted in a sudden increase in the resistance followed by an approximately constant decrease during the ethanol evaporation process. After approximately 3 min, the resistance decreased to between 1.8 and 7.2 times lower than the original value (Table 3). This significant decrease in resistance is likely explained by the SWCNT film densification, increased inter-tube contact and, consequently, an improvement in the percolation between SWCNTs. It is worth noting that the thermal compression integration process of SWCNT mats into polymer film did not cause significant changes to the electrical conductivity. The relationship between square resistance and optical transmittance for SWCNT mats with different thicknesses integrated into PE films are presented in Fig. 4a. For the optical transparency investigations, an uncoated pristine polymer film was used as a reference.

Since one of the potential applications of SWCNTs is devices based on cold electron field emission, we carried out measurements to demonstrate the applicability of SWCNT/PE film for such purposes. The procedure of the measurements is described

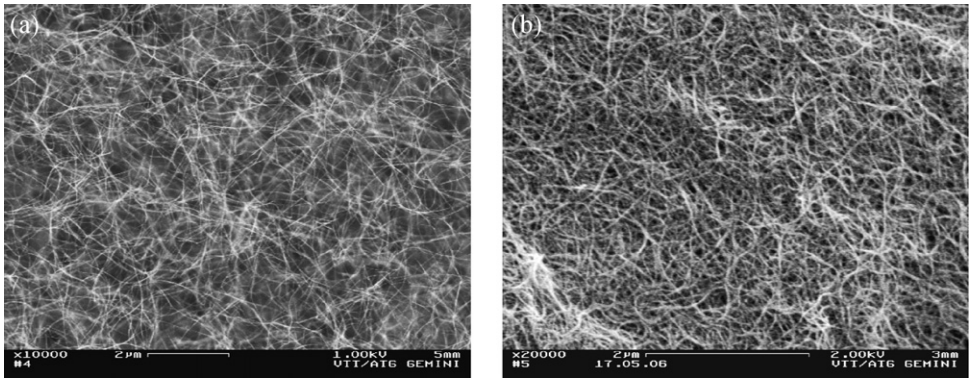

Fig. 3. Demonstration of SWCNT mat densification: SEM images of (a) the as deposited SWCNT mat and (b) the mat after treatment with ethanol.

Table 3
Effect on resistance of densifying SWCNT mats of different thicknesses with ethanol

Layer thickness before ethanol (nm)	24	35	100	500	2930
Square resistance before ethanol (Ω/□)	101700	17860	9400	4950	634
Square resistance after ethanol (Ω/□)	32000	3775	1860	690	350
Resistance decrease	3.2	4.7	5.1	7.2	1.8

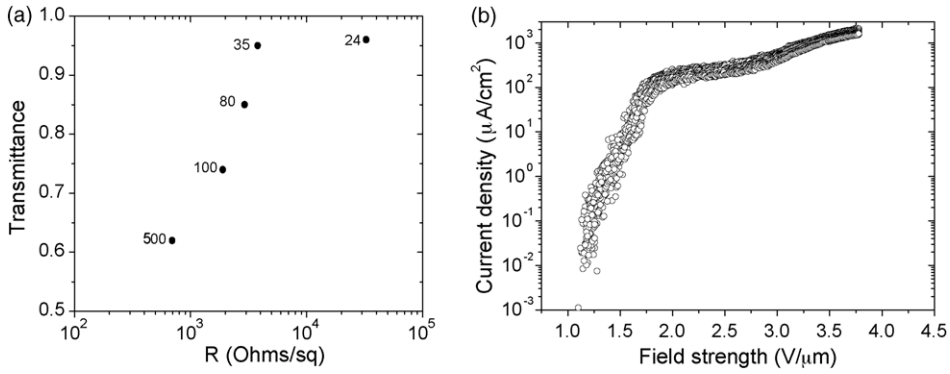

Fig. 4. Properties of SWCNT/PE films: (a) dependence of square resistance and transmittance (at 550 nm) on the CNT mats thickness; numbers are given in nanometers. (b) Field emission dependence of current density against the electric field strength.

in [6]. Fig. 4b shows the dependence of the current density against the electric field strength obtained during 10 runs. As one can see that the SWCNT/PE film exhibits a low field threshold of about 1.2 V/μm. Another advantage of the film is the presence of a clear current plateau, which is valuable for, for instance, flat screen displays, since the variation of the electric field between 1.7 and 2.7 V/μm does not lead to a significant change in the electron emission. Consequently, more variation is allowable in the component manufacturing process.

Another important and useful property of our SWCNT/PE films is their flexibility. The SWCNT/PE films were found to be bendable and could be repeatedly rolled and unrolled while retaining their transparency, conductivity and field emission properties (Fig. 5).

In summary, we have demonstrated a simple and efficient one step integration process for transferring SWCNT mats into PE thin films. These SWCNT/PE thin films have exhibited good optical transparency and conductivity as well as high mechanical flexibility. The electrical conductivity of the SWCNT mats was significantly improved by ethanol densification. Cold electron field emission measurements from a SWCNT/PE film showed a low field threshold and revealed the presence of a clear current plateau at electric field strengths between 1.7 and 2.7 V/μm.

Authors thank Dr. Unto Tapper for his assistance in SEM observation, Jussi Heikkonen for his help in preparing of some of the films and Dr. Sergey D. Shandakov for fruitful discussion. Financial support from the Academy of Finland and the Creative Research Initiatives Program supported by the Korean Ministry of Science and Technology are acknowledged.

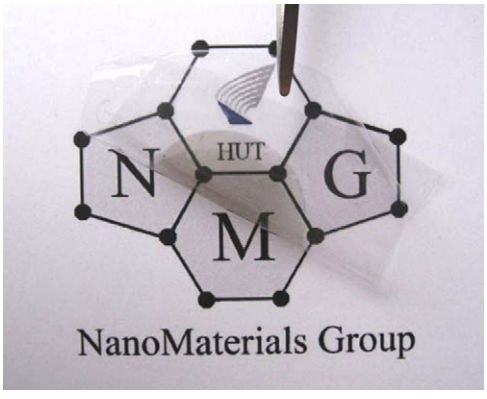

Fig. 5. Illustration of flexibility and transparency of a PE/SWCNT film produced according to the described method.

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