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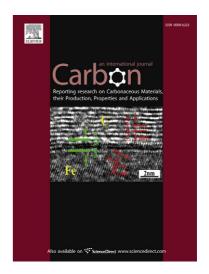
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Development of transparent, conducting composites by surface infiltration

of nanotubes into commercial polymer films

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ABSTRACT

Here we present a novel technique for the preparation of thin, transparent and conducting,

nanotube containing layers at the surface of commercially available polyethylene films. This is

achieved by the swelling of the polyethylene in nanotube/tetrahydrofuran dispersions, followed

by nanotube infiltration. These layers, typically 250 nm thick, display conductivities of up to

66 S/m, depending on the nanotube content. This results in sheet resistances of as low as 50

 $k\Omega/\square$ at optical transparencies of 80%.

1. Introduction

Optically transparent materials which can also conduct electricity are required for a wide range of

applications from electromagnetic interference shielding to transparent electrodes. In the past these

materials have been made, simply by coating glass with carbon or metal oxide films, most commonly

indium tin oxide (ITO). However, the standard production techniques are expensive and complicated [1].

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1

In addition the relative scarcity of indium has recently pushed up the price of ITO. Furthermore, with the rise of organic electronics in recent years it has become apparent that the development of technologies such as e-paper will require flexible, transparent conductors to act as electrodes. Due to its brittle nature, [2]. ITO is unsuitable for this application as its conductivity degrades significantly when strained [3]. Thus the development of new transparent conductors with conductivity which is stable against flexing and bending is critical.

In recent years, one of the main candidates for ITO replacement has been single walled carbon nanotubes in thin film form. Single walled nanotubes can be prepared as thin films with high transparency (~90%) and sheet resistances of a few hundred Ω/\Box [4, 5]. Highly conductive, strong and transparent nanotube-polymer composite coatings and films have also been prepared by layer-by layer (LBL) technique [6]. Due to their high conductivity, these thin films are potentially suitable for every application associated with transparent conductors including antistatic coatings and electrodes. However, these films are generally prepared from single walled carbon nanotubes (SWCNTs), which are very expensive. In addition, their adhesion to substrates and their electromechanical stability have not been well studied while their porosity will be an issue for some applications.

It should also be noted that not all applications require the high conductivities associated with SWCNT films. For example, applications such as electrostatic charge mitigation or electromagnetic interference shielding can be achieved with coatings of much lower conductivity [7-9]. Thus, we suggest that there are some advantages to transparent, conductive surface coatings based on relatively inexpensive multiwalled carbon nanotubes (MWCNT). These advantages would be enhanced for a coating that was well adhered to the substrate and which was non-porous.

Here we present a new approach whereby carbon nanotubes are incorporated into a thin surface layer within transparent plastic sheets by swelling and ultrasound assisted infiltration. Our processing technique involves soaking a thin polymer film in a dispersion of MWCNT in appropriate organic solvent under ultrasound. The combination of solvent and ultrasound causes the polymer film to swell, allowing nanotubes to diffuse in. This results in a thin, and so transparent, but conducting surface layer of nanotubes embedded in the polymer host.

2. Experimental

2.1 General Procedures

All chemicals where were purchased from Sigma-Aldrich unless specified otherwise. Thin MWCNTs (NC3100) were purchased from Nanocyl (www.nanocyl.be). Low density polyethylene (PE) film was purchased from BPI Packaging Limited. The ultra-sonic tip used was Model CV33 with ¼ inch tip, while the ultra sonic processor was a GEX 750. The ultra-sonic bath used was a Grant XB6 at 50 Hz. The scanning electron microscopy (SEM) images of the samples were obtained using a Hitachi S-4300 scanning electron microscope, which was operated from 5.0 kV to 20 kV depending on the sample used and coating required. For SEM non-conductive samples were coated with gold-palladium alloy to a coating thickness of 10-15 nm. Transmission values were measured using a Cary Varian 50 spectrometer. Electrical measurements were carried out using a Keithley 2400 sourcemeter. IV curves were measured using a two-probe setup. The potential difference across the sample was varied from 0 V to 100 V with intervals of one volt.

2.2 Preparation of polymer-nanotube composites

MWCNTs were dispersed in 10 ml of tetrahydrofuran (THF) at the following dispersion concentrations: 4mg/ml, 2mg/ml, 1mg/ml, 0.5mg/ml, 0.25mg/ml, 0.2mg/ml, 0.15mg/ml, 0.125mg/ml, 0.0625mg/ml and 0.03125mg/ml. Dispersions were then sonicated using a sonic tip for 5 minutes with a 1 second pulse (1s delay between pulses) and power regulated at 20% (of 750W). A 46μm thick, medium-low density, PE film was cut into strips (15 mm × 25mm), placed in the nanotube dispersion and sonicated again under the same conditions. Following this, each film was further sonicated for 30 minutes in an ultrasonic bath. Each film was then removed and washed in ethanol under bath sonication for 30 seconds. After drying polymer films were cut into strips of approximate dimensions, 15mm×2.4mm×46μm. Conductivity and transmittance have been measured for 5 different polymer strips and an average value was calculated for each case.

3. Results and discussion

In our work polymer—nanotube composite films have been prepared by soaking polyethylene films in MWCNT dispersions in THF at a variety of nanotube concentrations. Initially the composites have been analysed using scanning electron microscopy (SEM). Shown in Fig. 1A-C are SEM images of the film surfaces for films soaked in nanotube dispersions of increasing concentration, C_{Disp} , (0.125 mg/ml to 4 mg/ml). It is clear that the number of nanotubes on the surface increases with increasing dispersion concentration. Images of the cross-section of films fractured after dipping in liquid nitrogen are shown in Fig. 1D-F. From these images it is apparent that the nanotubes do not just form a surface coating but occupy a thin layer of the polyethylene film close to the surface. We believe that this is a thin polymernanotube composite layer formed by the diffusion of nanotubes into pores created by the swelling of the PE in the THF under ultrasound. While polyethylene is highly insoluble material, it can be swelled in certain organic solvents, particularly those with Hildebrand solubility parameters[10, 11] in the range 14-20 MPa^{1/2}[12]. As THF has a solubility parameter[13] of 18.5 MPa^{1/2} we would certainly expect polyethylene to swell in a MWCNT/THF dispersion. The fact that the nanotubes can intercalate into the swelled polyethylene suggests a strong mutual attraction as is expected given the hydrophobic nature of this polymer. This intercalation occurs on both sides of the polymer film.

Fig. 1 here

A more comprehensive SEM analysis was undertaken to measure the approximate thickness of the surface nanotube layer. For each composite film, the nanotube penetration depth, t, was estimated for forty different positions on the film. This data is presented in the Fig. 2A, inset, as a function of dispersion concentration. It is clear that the nanotube layer is approximately 250 nm thick for all composites except the one soaked in the highest concentration dispersion which had a film thickness of ~700 nm.

The optical transmittance was also measured for each film (Fig. 2A). As expected, the transmittance decreases as we increase the dispersion concentration. The transmittance, measured at $\lambda=550$ nm, as plotted in Fig. 2B, reaches a minimum of about 65% for the 4 mg/ml dispersion. We can use

this data, coupled with the measured film thickness, to calculate the optical absorption co-efficient associated with these nanotube films, α . The transmittance, T, is described by the Lambert-Beer law:

$$T = 10^{-\alpha(2t)}$$

The factor of 2 comes from the fact that there are nanotube layers on each side of the film. This expression has been used to calculate α as shown in the inset of Fig. 2B. It is clear from this figure that α increases with increasing dispersion concentration (C_{Disp}) before saturating at $\alpha \approx 1.5 \times 10^5$ m⁻¹ for $C_{Disp} > 1$ mg/ml.

We can use this data to estimate the volume fraction of nanotubes in the surface layer, V_f , by modelling the surface layer as a solid solution of nanotubes in the polymer matrix. Under these circumstances, the absorption coefficient of the surface layer can be approximated as: $\alpha = \varepsilon C_{Layer}$, where ε is the extinction coefficient of the nanotubes and C_{layer} is the average concentration of the nanotubes within the nanotube layer (mg/ml). We can relate C_{Layer} to V_f using: $C_{Layer} = \rho_{NT} V_f$, where ρ_{NT} is the nanotube density (~1800 kg/m³) [14]. This means that the volume fraction of nanotubes in the surface layer is given by $V_f = \alpha/\varepsilon\rho_{NT}$. Given that we have measured α , and know ρ_{NT} from the literature, we need only ε to calculate V_f . We find ε by assuming it to be invariant for solid solutions and liquid phase dispersions of MWCNTs in solvents (albeit at much lower concentration). We measured the absorbance of dispersions of thin MWCNTs in THF as a function of concentration allowing the calculation of ε =1220 ml mg⁻¹m⁻¹, a value of the same order as that of SWCNTs in solvents (3000-3500 ml mg⁻¹m⁻¹) [15, 16]. We can employ this to calculate the volume fraction of nanotubes in the surface layer as shown on the right axis in the inset of Fig. 2B. This demonstrates that while the thickness of the surfaces remains constant, the volume fraction of nanotubes increases with increasing dispersion concentration, saturating at ~8vol%.

Fig. 2 here

The polymer films were cut into strips of known width and length and the sheet resistance, R_s , measured by both a two and a four probe method. The sheet resistance as a function of dispersion concentration is shown in Fig. 3A. We see that R_s initially falls sharply with increasing dispersion concentration, saturating at less than $10^5 \ \Omega/\text{Sq}$ for $C_{Dis}>1 \ \text{mg/ml}$. The sheet resistance can be translated

into bulk conductivity, σ , using: $\sigma = 1/R_s t$. This is presented in Fig. 3B, illustrating the very rapid increase in conductivity as the dispersion concentration is increased toward $C_{Disp}\sim0.5$ mg/ml. At higher dispersion concentrations, the conductivity reaches values as high as 66 S/m ($V_f = 8.4\%$). This is quite a respectable value for a polymer-nanotube composite. A recent review has shown that only about 10% of composites reported to date display higher conductivities[17]. In fact, this value is only fractionally lower than results reported recently by Blighe et al for SWCNT based composites of similar volume fraction [18]. Blighe's results are notable as they claim that the composite conductivity is not limited by internanotube polymer tunnelling barriers. The similarity between the results of Blighe and those reported here suggest that the nanotubes in our composites may actually be in contact without the presence of any interfacial layer.

Fig. 3 here

To investigate this further we analyse our data within the framework of percolation theory [19]. For a composite composed of conducting particles in an insulating matrix, the conductivity is predicted to scale with volume fraction (for $V_f > V_{f0}$) as: $\sigma = \sigma_0 (V_f - V_{f0})^s$. V_{f0} is the percolation threshold; the critical volume fraction for the onset of current flow. For randomly arrayed rod-like fillers, the percolation threshold scales with the aspect ratio as $V_{f0} = 0.6d_{NT}/I_{NT}$ [20], becoming quite low for fillers like carbon nanotubes [17](d_{NT} and I_{NT} are the mean nanotube diameter and length respectively). The percolation exponent, s, is expected to depend on the dimensionality of the composite with calculated values of $s \approx 1.33$ and $s \approx 2.0$ in two and three dimensions respectively [17, 19]. σ_0 is a constant which depends on the conductivity of the filler particles. For most nanotube-based composites, σ_0 has been low due to the presence of polymer tunnelling barriers between adjacent nanotubes [17]. However, in the absence of such barriers [18], σ_0 can approach conductivity values found for nanotube only films, i.e. 10^4 - 10^5 S/m [21, 22].

The conductivity data as a function of volume fraction was fitted using the percolation equation as shown in the inset in Fig. 3B. A very good fit is obtained, confirming that the infiltrated tubes form a percolative network. From the fit we can extract values for $V_{f0} = 4\text{vol}\%$, s = 1.8 and $\sigma_0 = 1.2 \times 10^4$ S/m. A

percolation threshold of 4vol% is higher than expected for carbon nanotubes [17] and is suggestive of an aspect ratio of 15 which is much too low for the tubes used here. This may be due to the partial in-plane alignment of the tubes in the surface layer. It is well known that alignment effects can act to increase percolation thresholds for rod-like fillers [23, 24]. The measured value of percolation exponent of s=1.8 is very close to the universal 3-dimensional value of $s_{3D}=2.0$ [19]. This is slightly unexpected as the dimensions of our surface layer ($t<<|_{N_{\rm T}}$) would suggest the 2-dimensional value ($s_{2D}=1.33$) might be more appropriate. Most importantly, we measure $\sigma_0=1.2\times10^4$ S/m, a value which is higher than that found for most composites (see for example fig. 5 in Bauhofer et al [17]). In the absence of polymer tunnelling barriers, σ_0 is expected to be of the same order as the conductivity of a nanotube only film. This has been measured to be ~500 S/m for a film of MWCNTs similar to those used here [25]. That σ_0 is so high, strongly suggests that the nanotubes have intercalated into the film to form a network in such a way that adjacent nanotubes can form good electrical connections without the presence of a polymer tunnelling barrier. This is reminiscent of kinetic percolation [26], where connections between adjacent nanotubes can form due to attractive inter-nanotube forces. However, such phenomena usually results in a very low percolation threshold [17, 26] which is not observed here.

The maximum conductivity observed here was 66 S/m. This compares well with other surface treatments involving graphene oxide-silica composites on glass (45 S/m) [1] and MWCNT-silica composites (57 S/m) [27]. We do note however that these values are low compared to the most conductive polymer-nanotube composites. For example, **LBL** assembly enabled produce to poly(vinylalcohol)/(SWCNT + poly(sodium 4-styrene-sulfonate) layered coatings, which have displayed conductivities up to 4.15 x 10⁴ S/m [6]. There are also several reports about polymer composites based on a conducting polymer such as poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS). Recently [28-32], PEDOT:PSS has been combined with carbon nanotubes to produce transparent composite films with conductivities of up to ~1.6×10⁵ S/m [33]. However we believe the simplicity and relatively low costs associated with our infiltration method brings advantages to areas and applications where moderate conductivities are sufficient.

Conductivities at the level observed here result in a reasonable balance between sheet resistance and transmittance (Fig. 4) with the best observed film showing values of 50 k Ω / \square and 80% respectively. The reasonably low sheet resistance and high transparency of these films make these materials attractive for a number of applications. For example, electrostatic charge mitigation [9] requires sheet resistances in the range 10^6 to 10^{10} Ω / \square while electromagnetic interference shielding [7, 8] requires coatings with conductivity of at least 10 S/m. Our coatings have electrical properties that are suitable of both these applications, with the added bonus of reasonably high transparency and flexibility.

Fig. 4 here

4. Conclusions

Thus we have demonstrated a novel liquid phase method to infiltrate multiwall nanotubes into the surface layer of polyethylene films. This yields a transparent but conductive polymer composite. These polymer films displayed conductivities of up to 66 S/m which resulted in sheet resistances of 50 k Ω / \square at 80% transparency. We believe that our approach can be utilised for fabrication and processing of many various polymer-nanotube composite materials with unique properties and a broad range of potential applications.

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Figures:

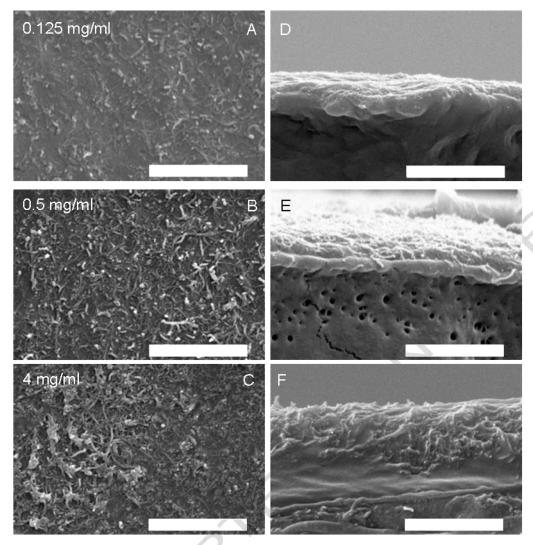


Fig. 1 - Selected SEM images of surface (A-C) and cross-section/surface edge (D-F) of films prepared for a range of MWCNT dispersion concentrations: 0.125mg/ml, 0.5 mg/ml and 4.0 mg/ml. In all cases the scale bar is 1 micron.

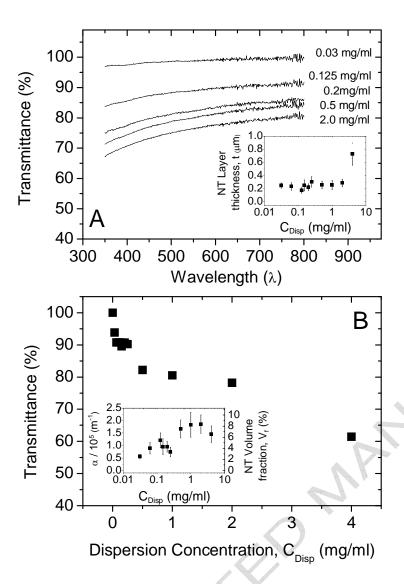


Fig. 2 - A) Transmittance spectra for some of the films used in this work. The films are labelled by the dispersion concentration. Inset: layer thickness as measured by SEM versus dispersion concentration. B) Graph of transmittance as a function of dispersion concentration. Inset: Film absorption coefficient versus dispersion concentration (left axis). Right axis: Nanotube volume fraction in surface layer versus dispersion concentration.

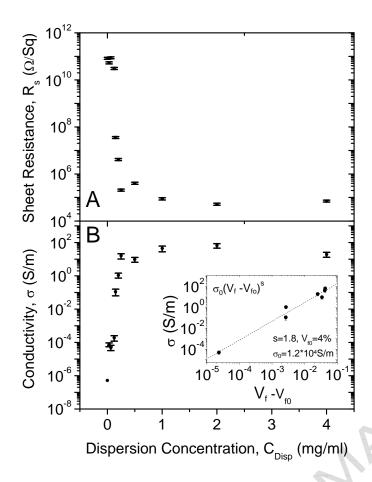


Fig. 3 - A) sheet resistance and B) conductivity of the surface layers versus dispersion concentration.

Inset: Percolation plot of conductivity as a function of nanotube volume fraction.

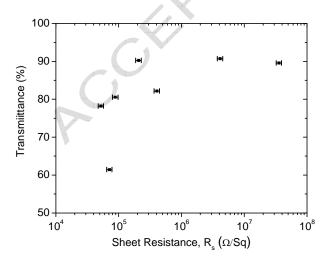


Fig. 4 - Graph of transmittance versus sheet resistance for some of the films prepared in this work.