Electrospun polyamide 11 (PA11) nanofibers films are used as a guide for the deposition of two-dimensional networks of multiwalled carbon nanotubes (MWNTs). This method allows for the manufacturing of transparent and electrically conductive thin films. It is demonstrated that the sheet resistance (Rs) and transmittance (T) decrease, as the films become thicker due to longer electrospinning times or larger fibers. The transmittance could be improved by fusing (melting) the fibers at moderate temperatures or impregnating the film with a resin, showing that light scattering rather than absorption by the MWNTs or the polymer was responsible for a low transmittance. As the number of MWNT deposition cycles increases, the Rs decreases with a constant transmittance. A fused 100 nm film obtained after 10 min of electrospinning of the 2 wt % PA11 solution shows Rs = 154 kΩsq⁻¹ and T = 83% after ten MWNT deposition cycles. A 95% transmittance was achieved after removing the polymer fibers by heating the glass plate in air (Rs = 440 kΩsq⁻¹ after five MWNT deposition cycles).

1. Introduction

Transparent and electrically conductive materials are required for numerous applications such as liquid crystal displays,[1] light emitting diodes,[2] transistors,[3] actuators,[4] sensors,[5] organic solar cells,[6] smart textiles,[7] and heated windows. Currently, commercially available transparent electrodes use glass panels coated with indium tin oxide (ITO), which suffers from several drawbacks. They are obtained by vacuum and high temperature processing, which is not suitable for many polymer substrates such as polyethylene terephthalate (PET), which are often used for touch screen panels and flexible devices. Furthermore, ITO films are brittle and will crack under a 2% strain losing their conductivity. Therefore, they are not applicable where a combination of conductivity and flexibility is required (e.g., antistatic coatings on fabrics or elastomers). Finally, the decreasing resources of crude indium induced a ten-fold price increase between 2003 and 2006,[8] which may limit the use of ITO in large-volume applications.

Carbon nanotubes possess outstanding electrical and mechanical properties (flexibility),[9] and conducting nanotube coatings can be produced at room temperature. Thin films manufactured from single-walled carbon nanotubes (SWNTs) show a sheet resistance in the range of 0.15–2 kΩsq⁻¹ at 80% transmittance.[10,11] In comparison, ITO coatings possess a sheet resistance of about 10 Ωsq⁻¹.[3] Therefore, SWNT films may replace ITO in many devices. However, they possess a similar limitation as ITO—a high cost. It is difficult to expect the use of SWNTs for coating window glass, making antistatic fabrics, or producing conducting plastic panels for spray painting in the foreseeable future. Multi-walled carbon nanotubes (MWNTs) constitute an attractive alternative because they are much more affordable (the cost is 2–3 orders of magnitude higher than SWNTs), which yields thin films of ≥ 250 kΩsq⁻¹ at 80% transmittance.[12,13] The implementation of MWNTs thin films remains very attractive in terms of cost/performance ratio, especially when considering short term and large volume commercialization. Unfortunately, only a limited effort has been dedicated to investigating conductive and transparent MWNT coatings.

Given the nanotubes tendency to form bundles, the manufacturing of uniform thin films has remained a challenge for both single- and multi-walled nanotubes. Generally, the nanotubes are dispersed in a solvent with the help of a surfactant. A film is then produced by spin-coating,[13] spraying,[5,7,14] rod-assisted coating,[15] casting,[12,16] or filtration[2,5,17] of the solution. However, the surfactant adsorbed on the surface of...
the nanotubes greatly affects the electrical properties. Geng et al. recently observed a significant conductivity increase by removing the surfactant using acid treatments. When acid treated SWNTs were used, low resistance (150 Ω sq⁻¹) films were produced. Surfactant-free electrophoretic deposition of MWNT coatings on nickel foils also led to an enhanced electrode performance of supercapacitors, for which no transparency is required. Limitations of the current techniques include (i) the necessity of a flat horizontal substrate, (ii) the use of a binder, e.g., surfactant or polymer that decreases the conductivity, and (iii) difficulties for scaling up to the industrial level.

The objective of our work was to produce MWNT coatings that would be a viable candidate to replace ITO, providing sufficient conductivity for most applications, but without the price tag and physical limitations of the current ITO or SWNT coatings. We used electrospun nanofibers of ~100 nm in diameter to guide the deposition of MWNTs and to create a two-dimensional network of nanotubes on the surface of glass by a surfactant-free self-assembly method.

2. Results and Discussion

The structure of the as-deposited films, obtained from a 2 wt% PA11 solution (130 nm average diameter) after 10 min of electrospinning and coated with acid-functionalized MWNTs in five deposition cycles, is shown in Figure 1a. It can be observed that the MWNTs are located on the fibers and not on the glass substrate, creating a conducting 2-D network at a low surface coverage. This is the principal difference between the technique discussed in this work and casting or spin-coating techniques. While in all cases a quasi-2D structure is created, the homogeneous dispersion achieved by conventional techniques leads to high percolation thresholds. In the case of nanofiber films, MWNTs are guided to form a percolated structure, even at very low concentrations. All fibers are coated with MWNTs, revealing a homogeneous deposition process that allows the formation of an MWNT network. The MWNT network structure remains even after polymer melting (Fig. 1b), which was used to fuse the fibers and provide a stronger binding of the nanotubes to the substrate. This is important since strong binding to the substrate could address potential health and safety concerns regarding free nanotubes. The change in contrast is probably due to the formation of a continuous film of polymer that, by retaining the electronic charges, appears white and leads to a strong contrast with the MWNT network. The electrical resistance and light transmittance of initial and fused (melted) films as a function of electrospinning time are shown in Figure 2. It appears that melting the films significantly improves their transmittance. With increase in electrospinning time, i.e., thicker mats, the resistance decreases due to the formation of a dense MWNT network. For long electrospinning times, the total film resistance decreases but its specific conductivity, i.e., normalized to the film thickness, also decreases (Table 1). This can be due to a filtering effect of the polymer fiber mat, because of which MWNTs cannot impregnate the mat through its entire thickness, leading to a lower specific conductivity. When the polymer fibers were fused, the resistance increased with electrospinning time (amount of polymer). Before melting, the connectivity between individual nanotubes is good due to hydrogen bonding between the carboxyl groups on the MWNT surface. However, after melting, polymer chains can separate the nanotubes, decreasing the connectivity. This phenomenon, observed in a similar way with surfactants, could explain why despite retaining the network shape (Fig. 1b), the conductivity decreases after melting the fibers. The gain in resistance after the melting process seems to be increasing with the amount of polymer. However, at very low polymer contents, a dramatic increase in resistivity is observed (Fig. 2), which could be
explained by the fact that in this case (very high MWNTs concentration as compared to the polymer content), MWNTs retain the melted polymer in their vicinity by capillary forces, which lowers the MWNTs connectivity.

The resistance increase associated with melting is however compensated by a large gain in transmittance. Figure 2b shows that the transmittance of pristine mats decreases rapidly with electrospinning time, reaching values close to zero after 120 min. The transmittance is partially recovered by melting the fibers. This effect is more pronounced for longer electrospinning times, due to the very large light scattering effect of thick mats that completely disappears upon melting. The transmittance of the pristine mat produced in 120 min was 0.3% (Table 1) before melting and 73% after. The effect of the number of MWNT deposition cycles on resistance and transmittance is shown in Figure 3. The nanofibers were spun from the 2 wt % polyamide solution (130 nm average diameter) electrospun for 10 min.

Table 1. Electrical and optical properties of nanofiber mats from the 2 wt % PA11 solution coated with five MWNTs depositions as a function of electrospinning time.

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because the surface coverage of fibers with MWNTs improves. A resistivity decrease of about two orders of magnitude was obtained by increasing the number of MWNT depositions from 3 to 10. Because the polymer concentration in this set of samples is very low, melting has a limited impact on the resistance. The transmittance remains at a constant value of 80% (within the confidence range of ±5% for one sample analyzed at different locations with a 200 μm beam) independent on the number of MWNT depositions (Table 2). This implies that the thickness of the MWNT layer has a very small effect on the transmittance and that light scattering by polymer nanofibers is primarily responsible for the reduced transmittance. Therefore, in order to obtain an optimal combination of resistance and transparency, one should work with short electrospinning times, small fibers, and a large number of MWNT depositions. A 100 nm film with $T = 85\%$ and $R_s = 176 \Omega \text{sq}^{-1}$ was obtained by ten depositions on the 2 wt % PA nanofibers-covered slide with subsequent melting. For the same transmittance, commercially available ITO and SWNT-coated glass have a resistance of $6 \Omega \text{sq}^{-1}$ and $0.7 \Omega \text{sq}^{-1}$, respectively. Therefore, if high conductivity is desired, our method could be used to produce SWNT films.

The effect of fiber diameter on the resistance and transmittance of initial and melted films obtained from different PA11 concentrations is shown in Figure 4. The films were produced by 10 min electrospinning and were coated with MWNT in five depositions. It appears that both resistance and transmittance of as-deposited films decrease with increase in fiber diameter. Table 3 shows that while the resistance of the films decreases with fiber diameter, their conductivity (normalized to thickness) remains approximately constant. Figure 5 shows that after melting, a glass slide coated with the largest PA11 fibers (540 nm) and five MWNT depositions still appears transparent with a transmittance of 67%, recovered from the 38% before melting. Melting the films leads to an improved transmittance due to a reduced light scattering from individual fibers. Upon melting, the samples with the largest fibers showed a significantly higher electrical resistance due to a disruption of the MWNT network and increased separation between individual nanotubes.

This series of experiments shows that while melting the films improves their optical properties, the electrical conductivity can be affected. In an attempt to overcome this problem, the films were impregnated with a polyester resin to match the refractive index of PA11 and reduce the light scattering effect. Figure 6a shows a film obtained from the 4 wt % solution, corresponding to the largest fibers (540 nm), producing translucent films due to significant light scattering. When the same film was impregnated with the polyester resin (Fig. 6b), it became highly transparent. The resistance of a 2 wt % film after five MWNT depositions showed a value of $450 \Omega \text{sq}^{-1}$ before and $4 \Omega \text{sq}^{-1}$ after impregnation. Therefore, this method, while giving high transparency cannot be considered as an alternative for melting the films since it increases the film resistance by an order of magnitude.

To further improve both electrical and optical properties of the films, the polymer was completely removed by annealing.
the films on glass in air at 450 °C (above the decomposition temperature of PA11) for 30 min. This allows direct fusion of nanotubes to the glass surface without destroying the 2-D network structure. As can be seen in Figure 5b, the transmittance of all the films was very high, reaching 96%. The resistance was somewhat higher (Rs = 440 kΩ sq⁻¹) than that of the as-deposited film (Rs = 258 kΩ sq⁻¹). Therefore, high-temperature annealing is an effective way to obtain highly transparent conductive films on glass and other inorganic substrates. A polymer with a lower decomposition temperature than PA11 can make the removal easier and enable transferring the 2-D MWNT networks onto fabrics and thermally stable polymers such as PVDF or PTFE. These films could be used as a replacement for ITO coatings or for building 2-D and 3-D architectures of conductive MWNTs in the active layer of solar cells[20] or supercapacitors.[19]

It is also interesting to note that it is possible to build electrically conductive bridges of suspended fibers over grooves on the surface, between standing posts, etc., thus enabling the application of these conducting thin films on surfaces of more complex geometries than just smooth glass slides.

3. Conclusions

Use of flexible mats of electrospun PA11 nanofibers coated with MWNTs enables the manufacturing of thin (0.1–1 μm) conducting 2-D networks. The advantage of the developed technique is that nanotubes do not form a uniform coating but a percolated network of MWNTs, guided by polymer nanofibers, thus improving the transparency of the film.

It has been demonstrated that melting or impregnating the films with a resin increases resistance but improves transmittance. Annealing in air at 450 °C increases transmittance to 96% with little effect on the resistance.

As the number of MWNT depositions increases, the resistance decreases to 150 kΩ sq⁻¹ with a constant transmittance of about 85%. It is concluded that the thinnest films, having the highest MWNT coverage, lead to the best combination of electrical and optical properties.

4. Experimental

**Materials**: PA11 (Rilsan®, BESVOA grade) and MWNT were provided by Arkema Inc. PA11 had a specific gravity of 1.05 g cm⁻³, a melting point of 180 °C and a decomposition temperature of 390 °C[21]. MWNTs were produced by catalytic chemical vapor deposition (CCVD) and showed diameter and length in the range of 10–20 nm and 1–10 μm, respectively.[22]. Formic acid (FA, 98%) was purchased from EMD chemicals. Dichloromethane (DCM, 99.9%) and 99% dimethylformamide (DMF), were purchased from Acros Organics. Nitric acid (70%) and 96% sulfuric acid were purchased from Sigma–Aldrich. The polyester resin (Castolite kit) was obtained from the Leco Corporation and glass slides (22 × 22 mm², 0.2 mm thick) were purchased from Fischer Sci.

**Electrospinning**: To produce nanofibers, PA11 pellets were dissolved in a mixture of FA/DCM (1/1 by volume) at the desired concentration, as described elsewhere[23]. A Nanofiber Electrospinning Unit (NEU) from Kato, Japan was used for spinning fibers at 10 kV with a distance of 15 cm between the electrodes in a horizontal syringe configuration. The syringe pump speed was adjusted to 20 μL min⁻¹. A set of six glass slides was taped on an aluminum foil, which was used as the collecting electrode. At half of the...
electrospinning time, the foil was rotated by 180° to limit the effects of local electric field inhomogeneities. The nanofiber-coated glass slides were then used as a substrate for MWNT deposition.

**MWNT Oxidation:** In order to achieve a strong interaction between the MWNTs and the polyamide fibers, carboxyl groups were grafted on the MWNTs to allow hydrogen bonding, as suggested by Kim et al. [24]. The carboxyl groups were created by an acid treatment following our previous work [25]. First, as-received MWNTs were immersed in a boiling mixture of nitric and sulfuric acids (1:1 by volume) for 10 min under reflux. The solution was then allowed to cool down for 30 min and the acid was removed. The collected MWNTs were rinsed with de-ionized water and centrifuged. This procedure was repeated (typically 10 times) until the solution reached neutral pH. The MWNTs were then dried at 70°C overnight and the resulting powder was used for further experiments. Material loss resulting from multiple purification steps decreased the yield by less than 5%. The electrical conductivities of the as-received and oxidized MWNT powders were found to be equal with a value of 10^4 S cm^-1.

The solution used for MWNT deposition was prepared by dispersing 10 mg of acid-treated MWNTs in 30 mL of DMF. The solution was ultrasonicated for 1 min using a Sonics Vibracell 500 W (Sonics and Materials Inc.). The resulting solution was stable over time (no settling observed over three months).

**MWNT Deposition:** In order to obtain an instant contact and avoid halo formation, the fibers were coated with the solution by pouring directly the solution on the fibers. The droplet of solution was placed on a clean glass slide and the nanofiber-coated glass slide was placed onto it. When the solution came in contact with the nanofibers, the MWNTs settled down instantly, possibly due to the remaining FA in the fibers, which by lowering the pH caused the nanofibers to aggregate. Therefore, after a brief interaction with the fibers (a few seconds), the solution was removed and the MWNT-coated slide was allowed to dry at room temperature for 10 min. As a consequence of the fast MWNT aggregation, we observed that while extended interaction time did not increase the MWNT coverage, multiple deposition cycles increased the coverage, and thus, the conductivity. The PA11–MWNT films were heated to either ambient (hotplate at 180 °C) or oxidize the PA11 fibers (air at 450 °C for 30 min, using a tube furnace).

**Equipments:** Scanning electron microscopy (SEM) was performed using a Zeiss Supra VP-50 field emission SEM. Thickness measurements were performed on a Zephyr NewView 6K profilometer, providing an z resolution of 0.5 nm. Electrical resistance was measured by a two-probe method using a Keithley system 196 (Keithley Instruments, Inc.). UV–Vis spectra were recorded with a PerkinElmer, UV/Vis Lambda 890 spectrometer, using an uncoated glass slide as a reference.

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