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Abstract

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Keywords

Controlled, Deposition, Polymer, Carbon, Nanotube, Composites, through, Inkjet, Printing

Disciplines

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Controlled Deposition of Polymer Carbon Nanotube Composites through Inkjet Printing

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Abstract—**The controlled deposition of polyaniline carbon nanotube composites by inkjet printing is reported. It is demonstrated that the sheet resistance and transmittance can be expressed in amount of composite and MWNT material deposited. The most efficient way for improving the sheet resistance while keeping the cost in optical transparency to a minimum is by increasing the total amount of material deposited, rather than increasing MWNT loading fraction.**

Inkjet printing; polymer; composite; carbon nanotubes

I. Introduction

Carbon nanotubes have attracted much attention since their discovery in 1991, and are investigated in a vast number of diverse fields. It is the unique properties of carbon nanotubes, such as their conducting or semi-conducting nature, that make them of interest for use in a range of applications, from composite materials to field-effect transistors [1]. They are, however, difficult to process from their as-produced state due to strong attractive interactions with each other, and their hydrophobic nature [2]. This so-called processing issue has been addressed using solution based approaches [2]. One of the advantages of using solutions is that they are easily adapted for different types of nanotubes, dispersants and solvents. These approaches include (but are not limited to) drop deposition, filtration, fibre spinning, spraying or inkjet printing [2-6].

Inkjet printing is an attractive processing method, as it is an “easy” relatively straightforward fabrication process, after all most of us use these printers on a daily basis for a variety of purposes. These printers operate by “drop-on-demand”, ejecting small volume (10^{-12} L) droplets of ink from nozzles to create patterns. Hence it is a useful method for deposition of tiny quantities of functional “inks”, where the patterns can be designed to perform either electrical, chemical, optical or mechanical function. Previously we have demonstrated that inkjet printing is a viable tool for processing polymer carbon nanotube composite materials.

In this paper we show that inkjet printers can be used to control the deposition of polymer composite materials allowing us to express the sheet resistance and transmittance as a function of polymer, nanotube and composite material deposited.

II. Experimental

A. *Materials*

Catalytic chemical vapour deposition produced multi-walled carbon nanotubes (MWNT) were obtained from Nanocyl S.A. (Belgium, batch no NFL60). Aniline (Aldrich) was distilled and stored at -4 °C prior to use. The highly water-soluble polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS) was polymerised and purified using in-house procedures.

B. *Preparation of “inks”*

The chemical procedure for the preparation of nanotube dispersions (“inks”) involved *in-situ* polymerization of aniline in the presence of PMAS stabilized MWNT by a rapid mixing reaction route. MWNT were dispersed in PMAS using ultrasonic treatment at 16 W for 120 s in pulsed mode (2 s on, 1 s off). Sonolysis of this duration did not significantly degrade PMAS. A 100 μL solution of 1 M ammonium persulfate (APS) in 1 M HCl was added rapidly to 5 mL aqueous dispersion of PMAS-MWNT and 0.08 M aniline in 1 M HCl, and stirred for 5 hours. The final aniline-to-APS molar ratio was 4:1, while the MWNT:aniline weight ratios were 0.6 and 1.35. The resulting dispersions were purified by 3 cycles involving washing with Milli-Q water and centrifugation. PMAS functions in a dual role as a nanotube stabilizer and as a molecular dopant during aniline polymerisation, which results in the formation of PAn/PMAS-MWNT composites. Stable dispersions were obtained for MWNT:aniline ratios 0.6 and 1.35, corresponding to 17.5% and 32% MWNT loading fraction, respectively.

C. *Inkjet printing*

Nanotube dispersions (concentration 10 mg/ml, temperature 25 ºC, viscosity 5.5 cP, and surface tension 72 mN/m) were inkjet printed using a Dimatix materials deposition system (Fujifilm Dimatix) with the standard piezoelectric nozzle voltage settings (16 V). The cartridges used for printing were MEMS-based, with 16 nozzles (20 µm diameter) spaced at 254 µm, each dispensing a droplet volume of 10 pL. Patterns were deposited onto flexible transparent poly(ethylene terephtalate) (PET) substrates using 15 and 20 µm dot spacing, corresponding to 667 and 500 dots per cm, respectively.

D. Characterisation

Sheet resistance measurements were carried out using a JANDEL four-point probe resistivity system (model RM2). UV-visible absorption and transmittance spectra were recorded using a Cary 500 UV-Vis-NIR spectrometer.

III. RESULTS AND DISCUSSION

The UV-visible absorption spectra for the stable dispersions at MWNT loading fractions 17.5% and 32.0% (by weight) are shown in Figure 1. Increasing the nanotube content results in a decrease in the intensity of the band at 450 nm (assigned to polymer), while absorbance above 600 nm (assigned to nanotubes) increases. The optical and electrical properties of highly conducting but light absorbing material such as carbon nanotube are affected by the amount of nanotubes deposited as demonstrated using line patterning [7]. Increasing the nanotube concentration reduces both the sheet resistance (R_S, more electrical pathways) and transmittance at 550 nm (T, more light absorbed). This is demonstrated by increasing the number of printed layers, the MWNT loading fraction and spacing between deposited drops.

A. Controlled deposition

The sheet resistance and transmittance of a single inkjet printed layer (drop spacing 15 µm) of a composite with 17.5% MWNT loading on PET are 2.5 kΩ/□ and 50%, respectively. This allows us to compare the optical and electrical properties as we change the amount deposited.

However, as inkjet printing involves the controlled deposition of drops onto a substrate it is also possible to calculate the amount of material deposited per area. The drop spacing value dictates the number of drops deposited per cm in x and y direction, n_x and n_y, respectively. For example, a drop spacing of 20 µm results in 500 drops per cm and inkjet printing a 1 cm x 1 cm feature would results in $n_x = n_y = 500$.

The drop volume of each drop (V_{drop}) is 10 pL (according to the manufacturer's specification). Combining this information with the number of layers printed (n_l) and the concentration of the ink (c_{ink}) allows us to calculate the amount of material deposited per area (D) as follows:

$$D = n_x\, n_y\, n_l\, V_{drop}\, c_{ink} \quad (1)$$

Hence, the amount deposited per cm^2 for a single inkjet printed layer (drop spacing 15 µm) of a composite ink at a concentration of 10 mg/ml as calculated by (1) yields D = 44.5 µg/cm^2.

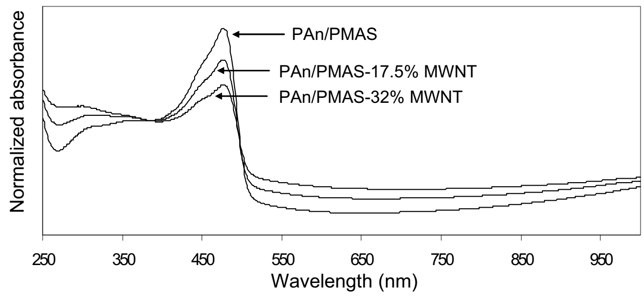

Figure 1. UV-visible absorption spectra (normalized) of PAn/PMAS solution and PAn/PMAS-MWNT dispersions with MWNT loading fractions 17.5% and 32.0% (by weight).

B. Carbon nanotube loading fraction

In comparison, inkjet printing a single layer of composite with 32.0% MWNT under similar conditions results in R_S = 2.0 kΩ/□ and T = 37%. The amount of material deposited is the same as calculated above. However, using the MWNT loading fraction (f_{MWNT}) this can be converted to amount of nanotube material deposited (D_{MWNT}) as follows:

$$D_{MWNT} = D\, f_{MWNT} \quad (2)$$

At 17.5% and 32% MWNT loading fraction the D_{MWNT} values are 7.8 µg/cm^2 and 14.2 µg/cm^2, respectively. Thus increasing the MWNT amount deposited by 6.4 µg/cm^2 results in a decrease in sheet resistance of 20% and a decrease in transmittance by 13%.

C. Multiple layers

Figure 2 shows that increasing the number of layers to 3 improves the electrical sheet resistance by a factor 2.5, at a cost of 20 % in optical transparency. The number of layers can be converted into amount of material and amount of MWNT deposited using (1) and (2), see also Figure 2. Thus doubling the amount of MWNT deposited in a decrease in sheet resistance by 40% and decrease in transmittance by a few percent.

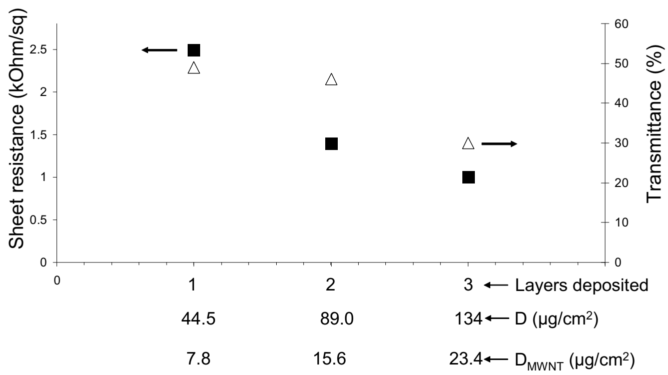

Figure 2. Sheet resistance (squares) and optical transparency (triangles) as a function of printed composite (10 mm x 35 mm, MWNT loading fraction 17.5 %) layers on PET substrate at drop spacing 15 µm. D and D_{MWNT} indicate the

amount of material and MWNT deposited, respectively calculated using (1) and (2).

This demonstrates that increasing the amount of material deposited by inkjet printing additional layers is a more effective way for improving the electrical properties compared to increasing the MWNT loading fraction as this comes at a lower cost in transmittance.

D. *Drop spacing*

We have already seen that increasing the MWNT loading fraction and increasing the number of layers deposited results in changes in the optical and electrical properties.

Figure 3 shows the effect of changing the drop spacing from 15 µm to 20 µm for the deposition of a single layer using an ink with a 32% MWNT loading fraction. Increasing the drop spacing decreases D (and D_{MWNT}) but increases sheet resistance and transmittance. Decreasing the amount of material deposited from 44.5 µg/cm^2 to 25 µg/cm^2 results in increases in sheet resistance and transmittance by 150% and 30%. Thus, while the transmittance can be improved significantly by increasing the drop spacing this results in a much larger cost in electrical properties.

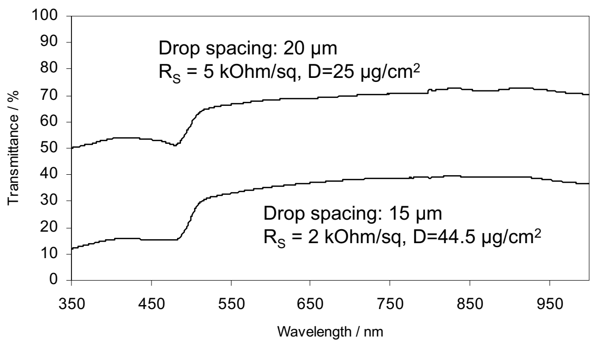

Figure 3. Optical transparency as a function of a single printed composite (10 mm x 35 mm) layer at 32% MWNT loading fraction on a PET substrate at drop spacing 15 µm and 20 µm. D indicates the amount of material deposited calculated using (1).

IV. CONCLUSIONS

We have described the controlled deposition of polyaniline carbon nanotube composites by inkjet printing. We showed that the sheet resistance and transmittance can be expressed in amount of composite and MWNT material deposited. The most efficient way for improving the sheet resistance while keeping the cost in optical transparency to a minimum is by increasing the total amount of material deposited. This improves the surface coverage resulting thereby increasing the number of electrical pathways which reduces sheet resistance. This paper contributes to the development of inkjet printing for the controlled deposition of materials.

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