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FLEXO AND SCREEN PRINTING OF GRAPHENE/ MULTIWALL CARBON NANOTUBE HYBRID

Vassiliki Belessi[1,2], Apostolos Koutsioukis[3], Theodora Philippakopoulou[1], G. Vlachopoulos[1], Vasilios Georgakilas[2]

[1]Department of Graphic Design and Visual Communication, Graphic Arts Technology Study Direction, University of West Attica, Greece

[2]Laboratory of Electronic Devices and Materials, Department of Electrical and Electronic Engineering, University of West Attica, Greece

[3]Department of Materials Science, University of Patras, Rio, Greece

Abstract

In this work, we present the development of conductive graphene water-based inks suitable for printing of several themes on different kinds of papers based on flexography and screen printing techniques. The inks were prepared by a hydrophilic graphene/carbon nanotube hybrid and suitable mixtures of resins. The as-prepared conductive inks were stable, highly conductive and their printing quality was comparable with that of conventional commercial inks. Especially, for flexography, the relationship between printing quality and the ink-carrying volume of the cells of the anilox roll and the pre-inking was investigated.

Keywords: *Conductive inks, Graphene, Flexography, Screen printing*

Introduction

Printing has gained increasing attention due to its definitive contribution to the wide field of flexible printed electronics and the great interest of researchers in functional printing. Screen printing, gravure, flexography and inkjet are the technologies that are mainly used in printed electronics (Cruz et al 2017; Ng et al 2019). Flexography has been used for the development of transistors, conductive grids on-label battery testers, drug delivery patches, printed batteries, piezoelectric pressure or bio and gas sensors, photovoltaics and other applications (Morgan et al 2018). An important advantage of this method is its lower cost compared to the quite similar gravure, where cylinders are of high cost and limited lifetime (Cruz et al 2017). On the other hand, screen printing is simple, inexpensive, one of the most important industrial printing techniques and can integrate easily different printing systems as for example digital printing system. It is used widely for advanced applications such as the printed circuit production, the printing of dye-sensitized solar cells or organic photovoltaics, the printing of biosensors or smart labels e.g. for augmented reality applications where we should note that flexography is also usable, the development of wearable electronics etc. (Wiklund et al 2021; Tsoukleris et al 2005; Singh et al 2022; Cruz et al 2017; Ng et al 2019).

However, the critical issue that needs to be noticed when applying printed electronics to these applications is the development of conductive inks (Koutsioukis et al 2017; Koutsioukis et al 2021, Belessi et al 2019). Up to now, commercial conductive inks are based mainly on metal (nano and micro particles), conductive polymers and carbon black or graphite while special interest has been given to graphene and graphene derivatives (Giasafaki et al 2022; Belessi et al 2019, Barmpakos et al 2021). Graphene is a monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice that has found numerous applications due to its excellent electrical and thermal conductivity, mechanical strength and optical properties. A great advantage of graphene is that it could be produced at low cost from an abundant natural material such as graphite although, up to now, an efficient and with high yield production method has not been established (Georgakilas et al 2005). Graphene nanosheets are single or few-layered nanostructures, highly hydrophobic (not dispersible in water) and only poorly dispersible in a few organic solvents that are not proper for the preparation of inks due to toxicity, high cost or environmental affairs. In the literature, several surfactants or dispersing agents have been used to provide graphene with the necessary dispersibility but in most cases the conductivity of the inks was negatively affected.

The purpose of this study was to prepare graphene water-based inks with high conductivity and accepted printability properties appropriate for flexography and screen printing. The inks were formulated using a hydrophilic graphene/carbon nanotube hybrid and suitable water-based mixtures of styrene–acrylate and acrylic resins (Georgakilas et al 2015; Koutsioukis et al 2017). The printed patterns were of high quality and precision. Especially, the screen printed patterns showed remarkable conductivities due to the thicker ink film.

Materials

Graphite, Multi-Wall Nano Tubes (MWNTs), sarcosine, 3,4 dihydroxy benzaldehyde and dimethyl formamide (DMF) were purchased from Sigma-Aldrich. The water-based resin emulsions (44.2% solid content) were products under development that contain mainly a mixture of styrene–acrylate and acrylic resins and provided from Druckfarben Hellas S.A. The printing substrates C 2846 (coated and calendared paper), smart-paper type 2 (special paper for printed electronics) and extra premium photo paper were obtained from IGT Testing Systems, Felix Schoeller Group and @work, respectively.

Preparation of Materials and Inks

The highly conductive and dispersible graphene/multiwall carbon nanotube hybrid (G/MWNT-*f*-OH) was prepared according to the methods reported in a previous work (Georgakilas et al., 2015). Briefly, 1.6 gr of graphene (G) was dispersed in 800 ml DMF and sonicated for 1h. Graphene dispersion was mixed with 0.4 g MWNT-*f*-OH (1 mg mL^{-1}). The mixture was stirred overnight and the hybrid G/MWNT-*f*-OH was isolated by rotary evaporation (65 °C, 120 rpm) and dispersed in 10 ml of water. This method was followed up to produce the necessary amount of the hydrophilic hybrid for the ink preparation.

One of them was formulated for screen printing (with total solids carbon/resin ratio 55/45) and the other two for flexography (with total solids carbon/resin ratio 55/45 and 70/30) (Table 1). Specifically, 1 g of the G/MWNT-*f*-OH was mixed with 0.97 g resin emulsion (44.2 % solid content), in totally, water volume was 9.9 mL to prepare ink suitable for flexography printing at solids carbon pigment/resin ratios of 70/30. That ink is symbolized as Flexo Ink70-30. Similarly, an ink at solids carbon pigment/resin ratios of 55/45 was prepared for flexography printing. 1 g of the G/MWNT-*f*-OH hybrid was mixed with 1.83 g resin emulsion (44,2 % solid content) and 12.1 mL deionized water. That ink is symbolized as Flexo Ink55-45. Finally, 1 g of the G/MWNT-*f*-OH hybrid was mixed with 1.83 g resin emulsion (44,2 % solid content) and 5 mL deionized water. That ink is symbolized as Screen Ink55-45. The mixtures were stirred for 2h to homogenize. For all inks, commercial resin emulsions were used to reduce their cost and improve their printability.

Characterization of Materials and Inks

The printing inks were fully characterized by various methods such as Scanning Electron Microscopy (SEM), Tunneling Electron Microscopy (TEM), electrical and rheological measurements. SEM images were collected using a Hitachi 6600 Field emission scanning electron microscope operating in the secondary electron mode and using an accelerating voltage of 5 kV. Microscopic analysis of the samples was performed using TEM (JEOL-JEM 2100). The values of V/I and sheet resistance (Rs) calculations of the hybrid, the printing inks and the printed patterns were measured by a 4-point probe system (Pro4 Resistivity System, Lucas Labs) and a Keithley 2400 Source Meter.

Printing

Initially, the graphene nanohybrid inks were applied on various papers, common or special, with the wired K-Bars (RK Print Coat Instruments Ltd., United Kingdom) numbered as 1 (6 μm wet film deposition) in order to choose the most appropriate types of paper.

Flexographic printing was performed with the IGT F1 printability tester. A printing plate was developed with respect to photopolymer hardness (70 Shore A). Four different anilox rollers (2.7, 4, 8 and 16 ml m^{-2}) and various printing speed (0.2 – 1.5 m s^{-1}) where used to determine the ink volume and speed effect, respectively. In all experiments, the anilox/printing force was 50 N and doctor blade pressure 6 N. Printability tests were first carried out by conventional ink in order to examine printing image design on flexographic plate and plate quality.

Preliminary screen printing tests of the conductive inks were performed using a manual screen printing machine (one colour, one station Kunshan), an aluminium screen printing frame with 90T mesh count (PE AM 90.48 PW, Saati) and a squeegee.

Results

The G/MWNT-*f*-OH hybrid was dispersed in mixtures of commercial water-based resins giving stable inks for flexo and screen printing. Figure 1 presents representative SEM and TEM images of the carbon hybrid. The Rs of the carbon hybrid and its ink were measured to be 9 Ohm sq^{-1} (e.g. 20 μL of 20 μg μL^{-1} of a hybrid suspension) and 16 up to 45 (depending on the resin content) Ohm sq^{-1}, respectively (Table 1). It was observed that the higher the total solids carbon/resin ratio the lower the Rs.

Table 1

Ink	Total solids carbon/ resin ratio	Pigment solids/ink solids	Resin solids/ ink solids	Total solids in ink (%)	Pigment solids in ink (%)	Ink Rs (Ohm sq^{-1})
Flexo Ink 70–30	70/30	0.70	0.30	12.04	8.42	16
Flexo Ink 55–45	55/45	0.55	0.45	12.12	6.70	45
Screen Ink 55–45	55/45	0.55	0.45	23.10	12.77	45

The viscosities of all inks were tuned to be printable for the two methods. The study of the rheological properties of the inks, that is not presented in this work, showed that they exhibit shear thinning properties in accordance with our previous work (Koutsioukis et al., 2021). In Figure 2 (left) are shown representatively printed patterns with flexography, using the G/MWNT-*f*-OH inks with the two different total solids carbon/resin ratio, 70/30 and 55/45, printed on the same IGT-coated paper. In Figure 2 (right) is shown a representative photo during the measurement of the V/I of a printed pattern with flexography. It was found that print quality and Rs values of the inks were improved for the flexo ink with the total solids carbon/resin ratio of 70/30 compared with that of 55/45.

Also, the effect of wetting of the printing plate was examined by the pre-inking process of the plate before printing, using the ink with the total solids carbon/resin ratio 55/45. The time between pre-inking and printing was critical because of ink drying. It was found that pre-inking increases the amount of applied ink and so the print quality (Figure 3). Furthermore, the ink-carrying volume of the cells of the anilox roll was shown to have a

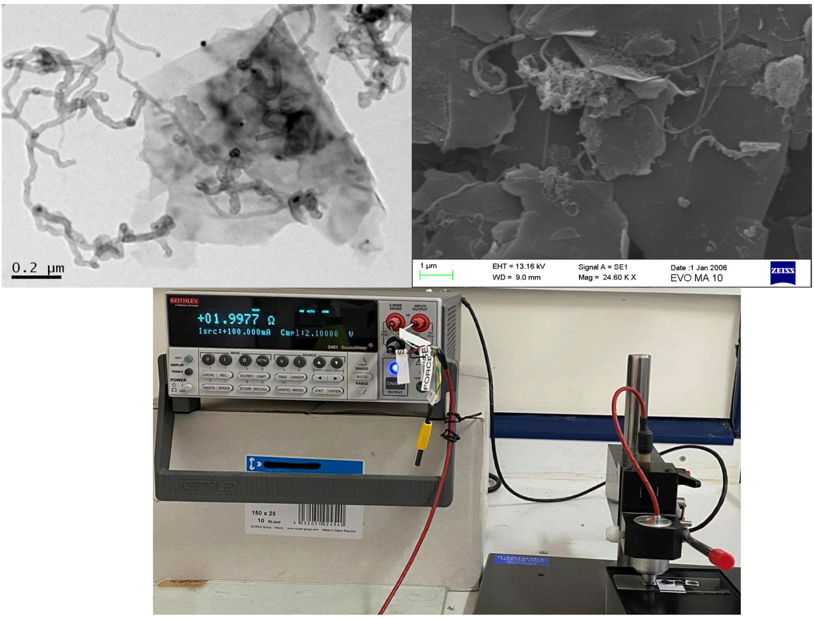

Figure 1. Representative TEM (Up and left) and SEM (Up and right) images of the carbon hybrid (Down) Measurement of the V/I of the hybrid

dominant effect on the print quality and affects ink film thickness. Specifically, the higher the anilox volume of the cells the better the print quality. Thus, it was chosen for all experiments the use of the anilox with a volume of 16 ml m^{-2} and pre-inking before all experiments. The Rs values of the flexo printed patterns were deviated between 2.3 and 44 kOhm/sq depending on the printed structure (e.g. the width of line). The Rs values are high due to the low thickness of the printed patterns (< 1 μm) but can be decreased when multilayer printing is applied (Ng et al 2019). Finally, various printing tests with the water-based carbon nano ink were carried out and found that the effect of printing pressure and printing speed had no significant effect on print quality.

The composite hybrid was used for the development of an ink, with total solids carbon/resin ratio 55/45, suitable for screen printing. This method has become a reliable and accepted printing solution for the application of conductive inks, facilitating high volume and low-cost production (Cruz et al 2017). Various structures like antennas, meanders or other simple symbols have been designed from our group, and found that they were easily fabricated using the screen printing method. Representative photographs of the screen printed patterns using the G/MWNT-*f*-OH nanohybrid are shown in Figure 4. The Rs of the screen printed patterns were below 2.5 kOhm/sq, mainly due to the thicker screen printed layer compared to flexography (Ng et al 2019).

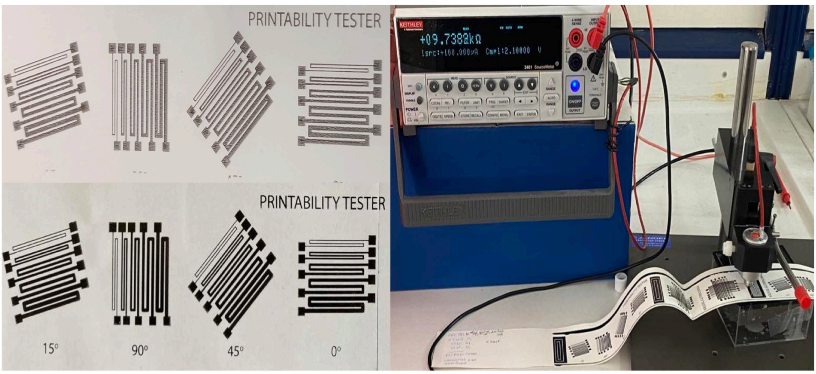

Figure 2. Flexography printed patterns, on the same paper, using the G/MWNT-f-OH hybrid with total solids carbon/resin ratio (left and up) 55/45 (left and down) 70/30. (Right) Measurement of the V/I of the printed pattern (with total solids carbon/resin ratio 70/30)

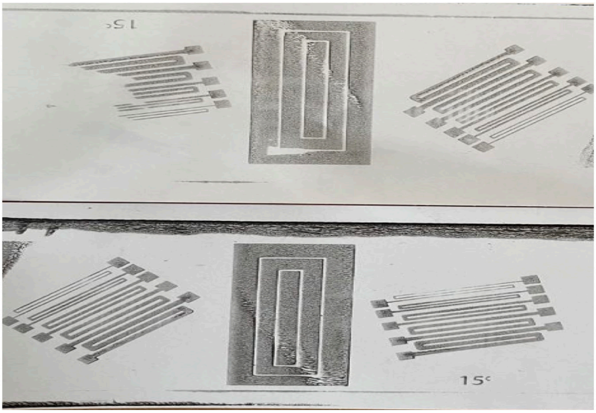

Figure 3. Flexography printed patterns, on the same paper,
using G/MWNT-f-OH hybrid with total solids carbon/resin ratio 55/45 (up)
without pre-inking and (down) with pre-inking

Figure 4. Representative screen printed patterns using the G/MWNT-f-OH hybrid
with total solids carbon/resin ratio 55/45 printed on (left) smart-paper type-2
and (right) extra premium photo paper

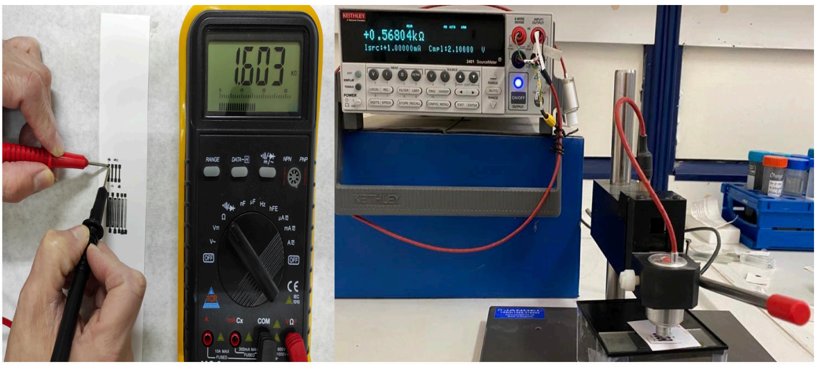

Figure 5. Various V/I measurements of the screen printed pattern

Conclusions

The as-prepared highly conductive inks were storage stable and printable. Higher Rs values were received for the flexo printed patterns compared to screen printing. Also, it was found that pre-inking increases the print deposition and the print quality.

Usually, stabilizers are required to prevent agglomeration in most inks, and also post-print treatments are necessary, but none of them was demanded in this work. The key property for achieving high-quality conductive printing inks was mainly the excellent dispersibility of the graphene/multiwall carbon nanotube hybrid.

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