Ink innovation with graphene

Rob Haslett and David Gibbs, of Haydale Ltd. outline the potential of graphene for use in printing and coating.

While advances are being made in exploiting the properties of graphene sheets, single layer graphene is currently very expensive to make and manipulate. It is also becoming clear that stacks of graphene sheets, known as graphene nanoplatelets, can radically transform existing materials when they are added as part of a solid composite or liquid dispersion and that the resultant materials can be cost effective across a range of applications from polymers to conductive inks.

Graphene is inert and does not readily mix with other materials. It must first be appropriately surface-treated or functionalised so that the end product can take full advantage of its superior properties. Functionalisation adds compatible chemical groups to the material surface which in turn enables efficient dispersion of the graphene nanoparticles. It is full dispersion that enables the final product to have an improved performance. Haydale’s HDPlas® (patent pending) process offers the most effective method of achieving nanomaterial functionalisation and harnessing the true potential of graphene to create high quality improved performance products.

Other functionalisation processes use an aggressive acid approach which can damage the graphene structure, also additional steps are needed to wash and dry the final product using significant amounts of energy while contaminants often remain. These processes also require different reagents for each functionalisation type and can be hard to control. The HDPlas® process is by contrast a dry approach that uses a low temperature plasma to perform the required functionalisation in a single step, with a wide range of control over the type and level of functionalization, using the same low energy process for adding a range of functional groups with no environmental waste issues.

Research collaboration

In order to generate new inks and coating applications for its functionalised graphene, Haydale has implemented a formal funded collaboration agreement, with the Welsh Centre for Printing and Coating (WCPC) at Swansea University, to enable long-term research and development projects that result in unique and market-driven applications. The way this works is that Haydale supplies WCPC with functionalised graphene and they create new prototypes which Haydale then market and manufacture if appropriate.

Haydale has worked with WCPC to develop and validate all its inks and printed products so far.

Conductive inks and coatings

Electronics has traditionally used copper tracks on rigid or flexible circuit boards to form the interconnection between components. Although commonly known as Printed Circuit Boards (PCBs), these are fabricated using a complex multi-step process where the interconnect pattern is applied using an optical (or laser) mask-curing process followed by chemical etching and then mask removal.

The idea of using a simple one-step printing process is very attractive since it reduces waste, time, complexity and, ultimately, cost. Inks can also offer other benefits such as better flexibility and the ability to be applied to a wide range of surfaces or items. Conductive inks have been available for some time based on graphic carbon, metallic flakes and, more recently, nanoscale metallic particles. Each of these inks have limitations, however, which restrict them to specialist applications: carbon-based inks have been poorer conductors when compared to metallic-based inks (e.g. copper and silver), which, despite their performance, are more expensive. Furthermore, the market price of silver rapidly fluctuates, making cost control extremely difficult in a manufacturing environment.

The addition of functionalised graphene has allowed Haydale to increase conductivity by a factor of more than four in comparison to a typical graphite ink. Haydale now sells a solvent-based graphene ink with a surface resistivity value of 12 ohms per square (normalised to 25μm ink thickness). While this does not yet compete with metallic-based ink, it does open up several significant applications. Being non-metallic, the ink is environmentally benign, with no special recycling requirements and is compatible with biological systems. The Haydale ink is designed for screen printing and works with a wide range of polymer substrates.

One commercially interesting application is a low profile, low cost, easily applied, multi-directional strain sensor. A series of thin tracks are printed onto a plastic substrate in different directions; the substrate is then bonded to the item being measured, a steel plate for example. Each track is then monitored for end-to-end resistance; any changes indicate applied stresses to the system.

Another application with great potential is single-use biological sensors, one example of which is blood glucose monitor test strips for diabetes management. Haydale is part of a project funded by the European Union’s M-ERA.Net, in a collaborative venture with Fraunhofer IBMT, Sauерessig, AlCuris and cellasys, aiming to print graphene electrodes with biofunctional coatings on large-area polymer foils via a roll-to-roll process, similar to the printing of newspapers. Through the development of this high-speed manufacturing process, the project is set to enable mass fabrication of graphene-based biosensors for the first time.
resulting in significant reductions of manufacturing costs for a wide range of medical applications such as detectors of pesticides, airborne pathogens, drug residues and antibiotics, glucose monitors and other health screening devices.

The project will undertake several steps to achieve this development over the three year period, including the production of a biocompatible, electrically conductive graphene ink (to be provided by Haydale) for rotogravure printing, and a fabrication method for micro (<10 μm) patterning of gravure printing cylinders. The project outcome will be a commercially developed roll-to-roll process and production line for the surface functionalisation of large polymer foils by gravure printing of a micro-patterned graphene/protein multiplayer, and will provide a proof of suitability for the printed multilayer for two different biosensor applications.

Carbon-based conductors also allow simpler construction of devices using new organic light conversion materials such as Organic Light Emitting Diodes (OLEDs), Organic Photovoltaics (OPV) and Organic Photodiodes (OPD). Haydale is collaborating with organisations that specialise in these areas and is creating multilayer devices that can use printing processes for their fabrication.

**Pressure Sensor**

This is the first full product created under the research collaboration agreement with WCPC. A variant of the conductive ink, which is far less conductive in the direction parallel to the substrate, was created. However, when two coated surfaces are assembled facing each other, the resistance between the coatings varies according to the pressure in a repeatable and linear way, a property known as Piezoresistivity. This behaviour allowed WCPC to produce a prototype sensor sheet using multiple electrodes under the coatings on each sheet so that pressure can be simultaneously monitored in real-time at a grid of points across the sheet.

Due to the nature of the ink, the sensor assembly is extremely simple to produce. First, a conductive pattern is printed onto a sheet of plastic such as polyethylene terephthalate (PET); then a continuous coat of specially developed graphene Piezoresistive ink is applied; and finally two sheets are assembled together for connection to monitoring electronics. The result is a flexible plastic sheet thinner than a credit card (which can be made into almost any size or shape) that will continuously map pressure at many points across its surface.

This opens the way for a whole range of application areas that are now being explored, such as:

- Security flooring that detects intruders;
- Shelves that ensure displayed valuables are not touched;
- Beds that monitor a patient’s presence and movement, or mats that help in post-operative convalescence;
- Floor sensors that assess the gait or stance of athletes, while pads could check their grip on rackets etc.;
- Industrial users can record pressure profiles between surfaces without the need to drill holes; and
- Footfall can be assessed, e.g. in shops, without the use of video cameras.

The sensor was launched at the end of September 2015 and partners are being sought across many of these market areas to develop customer focussed solutions for which Haydale will supply sensor sheets.

**Future Developments**

Haydale and WCPC are also working on other applications and ink products such as conductors and heaters that are stretchable for use in the fast growing area of wearable electronics. Here graphene’s conductive properties can once again be applied to a host material, in this case a stretchable polymer.

Other projects include exploring water-based inks following a big trend in graphic inks towards materials that are easier to use and less of a problem to dispose of.

**About the authors**

Rob Haslett is the sector manager and David Gibbs the product manager of Functional Inks at Haydale.