Flexographic printing is promising for large-area electronics due to high print-speed and roll-to-roll capability. There have been recent attempts in using graphene as an active pigment in inks, most notably for slower techniques such as inkjet and screen printing. However, formulation of graphene-enhanced inks for high-speed printing and its effect on key metrics have never been investigated. Herein, graphene nanoplatelets (GPs) are incorporated to a conductive flexographic ink without compromising the rheological properties. An industrial scale at 100 m min−1 is printed on paper and polyethylene terephthalate (PET) substrates using a commercial flexographic press, and statistical performance variations are investigated across entire print runs. It is shown that GP-incorporation improves sheet-resistance ($R_s$) and uniformity, with up to 54% improvement in average $R_s$ and 45% improvement in the standard-deviation on PET. The adhesion on both the substrates improves with GP-incorporation, as verified by tape/crosshatch tests. The durability of GP-enhanced samples is probed with a 1000 cyclic bend-test, with 0.31% average variation in resistance in the flat state on PET between the first and last 100 bends, exhibiting a robust print. The statistically scalable results show that GP-incorporation offers a cost-performance advantage for flexographic printing of large-area conductive patterns without modifications to traditional high-speed graphics printing presses.

1. Introduction

Printing is a mature industry ubiquitously utilized for a wide range of textual and aesthetic applications. Many developments in printing technologies since the Gutenberg press, developed in the 15th century, has seen diversification of the printing process beyond mass reproduction of text and graphics. Incorporating electronically functional materials into ink systems is relatively recent,[1–4] allowing printing to be used as a scalable additive manufacturing process for the fabrication of functional structures and devices on a range of substrates including paper and polymer.

2D materials exhibit a diverse set of properties which has made them attractive as the functional pigment in inks, as it opens up a wide scope of applications.[5–11] The electrical conductivity and environmental stability of graphene make it appealing as an additive or alternative to the traditional pigments used for printing conductive patterns. Specifically, the use...
of graphene offers potential performance and economic benefits over carbon- and metal-based inks, respectively. Graphene-enhanced inks occupy the middle ground between metallic inks and carbon-based inks when considering price/performance factors, increasing the scope of applications of functional printing for a range of large-area applications, such as interactive touch surfaces. Additionally, the incorporation of graphene in inks and composites has been shown to introduce novel properties,[12] improve electrical conductivity,[13] and mechanical durability,[14] all of which are important considerations for functional printing. Thus far, the formulation of inks containing graphene has largely been aided by the earlier development of liquid phase exfoliation of graphite[15–18] and relevant solution processing techniques.[18] The majority of reports on graphene-based inks have focused on laboratory-scale inkjet and screen printing.[4,5,19,20] Although these techniques lend themselves to rapid prototyping in a laboratory environment, they do not give insights into how well these approaches can be scaled up for commercial exploitation.

There are two dominant traditional high-speed roll-to-roll (R2R) graphics printing technologies suitable for scaled-up functional printing. Among them, gravure printing is a “direct” patterning process where ink is transferred directly on to the substrates from a gravure roller containing the print image. Flexographic printing, on the other hand, is the traditional, counterpart “indirect” printing process. This involves ink application by an anilox roller, which is then transferred to an image plate before deposition on to the substrate. There have been several attempts at prototype R2R printing demonstrations using graphene-based inks, most notably, by gravure printing.[6,21,22] Secor et al. was the first to demonstrate gravure printing of graphene-based inks on flexible Kapton substrates, displaying high-resolution conductive patterns.[6] Although this was an important milestone in graphene-based inks for R2R printing, it was only demonstrated on a small laboratory scale at a speed of up to 18 m min⁻¹, and without critical analysis into the ink formulation, printing process, and post print examination.

Hence, there remains a gap in understanding of the use of 2D material-based functional inks in a high-speed, commercial-scale manufacturing environment.

The flexographic printing process begins with ink from the trough filling the engraved cells of the anilox roller. The thickness of the ink layer is metered by a doctor blade[23–25] (Figure 1a,b). The ink transfers from the anilox roller to soft, flexible printing plates mounted onto the printing cylinder. The plates have the relief of the image to be printed protruding from the surface (Figure 1c(iii)). The ink only transfers to the raised image areas of the plate, which as the cylinder rotates is then transferred on to the substrate. This is shown in the photographs in Figure 1, Supporting Information. The ink transfers only to the raised image areas of the plate, which as the cylinder rotates is then transferred on to the substrate, as seen in the photographs in Figure 1, Supporting Information. This process repeats and with a constant substrate feed (Figure 1c(iii)), is capable of reaching speeds in excess of 100 m min⁻¹ for functional material printing, typically with <1 μm print thickness,[25,26] Inks used for flexographic printing typically have a low shear viscosity between 1 and 2 Pa.s, and the printing is usually conducted under atmospheric conditions (~25 °C).[25] We note that changes in factors such as temperature and humidity can have some effect on the printing, as a result these are often controlled. Crucially, flexographic printing is significantly less expensive than gravure printing due to the use of image plate, making it most attractive for large-scale functional print manufacturing.

In this work, we formulate a graphene-enhanced ink by using GP as an additive in a commercial carbon-based flexographic ink. We print our formulated ink using an industrial-scale flexographic printing press at speeds of up to 100 m min⁻¹ on both paper and PET substrates, producing kilometres of printed patterns without any modification of the printing press. We analyse the effect of GP-enhancement by statistically probing the inter- and intrasheet print resolution, uniformity, and sheet resistance across the entire print run and also the ink adhesion to the

![Figure 1. a) 3D and b) 2D schematic representation of the flexographic printing process. c) Photographs showing different parts and stages of flexographic printing on the commercial press in this work, left to right: substrate feed, printing cylinder, the print run on paper going through the press, drying of print, and finally rewinding of the roll.](image-url)
substances. Our results indicate that addition of GP improves all of the above performance metrics, with a cost/performance advantage when compared with non-GP alternatives.

2. Results and Discussion

We obtain water-based, commercial conductive carbon ink (Figure 2a inset) from Novalia Ltd., which is designed for high-speed R2R flexographic printing. The ink has a solid content of 70–74% which comprises of conductive carbon pigment and an acrylic-based polymeric binder which dissolves in mildly basic (pH ~ 8) conditions. We modify this ink by incorporating GP in powder form (NGP03, Perpetuus Advanced Materials). The GP powder we use consists of few-layer graphene structure with oxygen functionalisation and a zeta potential of −45 mV, which makes it easier to disperse in solution. The flakes go up to a few micrometers in lateral size. We homogeneously incorporate it in the ink using the method described in the Experimental Section. Figure S2, Supporting Information, shows the effect of different levels of GP on the sheet resistance of a web coated sample. We find that the addition of 2.5 wt% delivers a balanced compromise across improvement in conductivity, impact on ink viscosity/rheology and cost. We therefore use this concentration for the flexographic ink formulation.

For flexography, the most common commercial conductive ink formulations are based on carbon and silver. [27] Commercial pricing for carbon-based conductive inks ranges between $50 and $200 per kilogram. [28] The pricing of silver-based inks, on the other hand, is more volatile, with the price per kilogram being significantly affected by fluctuations in the market price of silver pigment. At present, the cost of a silver-based flexographic ink ranges between $1500 and $2000 per kilogram. [28,29] While silver-based flexographic conductive inks typically offer up to three orders of magnitude lower sheet resistance compared with their carbon counterparts (5–15 Ω/cm² vs 20–30 kΩ/cm²), the price and requirement for sintering make them unsuitable for low-cost, large-area applications requiring ~10–15 kΩ/cm² sheet resistance. A moderate improvement in sheet resistance from traditional carbon-based inks will allow more complex track geometries and greater linear length to be printed, without a notable increase in the total printed area or cost. From this perspective, our addition of 2.5 wt% GP in this work results in an overall increase of only ~3% of the carbon raw material cost.

After ink formulation, we conduct Raman spectroscopy to determine the effect of the addition of 2.5 wt% GP-powder to the commercial ink. For this, we isolate the pigments from the carbon-based and graphene-enhanced inks and deposit them on a Si/SiO₂ wafer; see Note 1, Supporting Information, for more experimental details. We carry out five measurements from randomly chosen locations on the samples and find no discernible changes when their typical Raman spectrum are compared (Figure S3, Supporting Information). This is likely due to the very low concentration of GP in the graphene-enhanced ink with respect to the original conductive carbon pigment.

In contrast, we observe a change in the ink viscosity after the addition of 2.5 wt% GP-powder. The viscosity versus shear rate of 0 and 2.5 wt% GP inks are shown in Figure 2a. GP-enhancement increases the starting viscosity of the commercial ink by 92%, from ~1.3 to ~2.5 Pa.s. This is close to the ideal viscosity range

![Figure 2.](image)

Figure 2. a) Viscosity against shear rate for the commercial conductive ink (0 wt%) and the graphene enhanced ink (2.5 wt%), inset shows a photograph of the ink. b) Log–log plot of the viscosity against shear rate to allow the extraction of the parameters of the power–law model. c) Bar graph representing change in sheet resistance upon the addition of graphene to the commercial ink on flexographically printed samples on paper and PET. Scanned fiducial pattern on d) paper and e) PET, with corresponding optical microscopy image of the 0.1 mm line (scale bar is 50 µm). f) Microscope image of the edge of the GP-enhanced print on PET (scale bar 20 µm). We use the values measured above and below the mean line to calculate the LER. The same analysis was conducted for all of the samples.
for high-speed flexographic printing, where the recommended starting viscosity is between 1 and 2 Pa.s.\[^{[25,30]}\] We note that there is some tolerance beyond this range as the quality of print is dependant on many external, non ink-based factors.\[^{[10]}\] However, inks that fall very far outside of this viscosity range will cause improper prints, including deleterious effects such as poor print resolution and incomplete print coverage.

It is also imperative for flexographic inks to be shear thinning to aid the ink to fill the cells of the anilox roller and be transferred between the rollers efficiently when under shear stress. We therefore analyze the power–law fit of the viscosity (\(\eta\)) against the shear rate (\(\dot{\gamma}\)) which when applied to fluids, gives insights into its behavior under shear (Figure 2b). The power–law model can be mathematically expressed as: \(\eta = K\dot{\gamma}^{n–1}\), where \(K\) is the consistency factor and \(n\) is the power law index. The value of \(n\) gives information on the ink such that when \(n = 1\), the ink exhibits Newtonian behavior, when \(n > 1\) the ink is shear-thickening and when \(n < 1\) the ink is shear thinning.\[^{[31]}\] The numerical values for the power–law measured for the two inks are presented in Table S1, Supporting Information. The resultant power–law fit for the inks show a good fit (Figure 2b), with \(R^2\) values >0.97 across the full range of the applied shear stress. The value for \(n\) is <0.8, which indicates shear-thinning behavior for both the inks. This confirms that despite the addition of 2.5 wt% GP, the ink is still shear-thinning and hence, does not require any further modification for high-speed flexographic printing.

We therefore conduct our printing comparison between the original carbon-based commercial ink (0 wt% GP) and the GP-enhanced ink at 2.5 wt%.

For the flexographic printing we conduct in this work, we use a coarse anilox roller (60° hexagonal pattern, 200 lines.cm\(^{-1}\)) with a large cell volume (8 cm\(^3\) m\(^{-2}\)). This is to ensure sufficient ink deposition as we print a single layer in our experiment. With appropriate print set up, we note that successive deposition of multiple layers would also be possible with these inks since it has the same rheological requirements. Our printing is conducted using a commercial Nilpeter FB3300, eight-unit flexographic printing press; Figure 1c.\[^{[12]}\] This is a commercial flexographic printing press and is widely used in the graphics industry, including for printing product packaging labels. The printer set up we use allows for heated drying directly after printing to remove the bulk of the ink solvent before the print passes over a path roller, and again later on the press to ensure the print is completely dry before rewinding into a roll; Figure 1c(iv, v).

The pattern we print, shown in Figure S4a, Supporting Information, comprises fiducial patterns that allow evaluation of the print quality and touch pads with a PCB connection point to make a capacitive touch sensor. For the print runs, we load 1–1.5 kg of ink into the trough and use up to 300 m of substrate to set up the impression and optimise the printing parameters. We print \(\approx1000\) m of sample per print run, which is effectively a trial run, as once set up, many kilometres can be printed in a single run. We note that both inks print on both substrates at a speed up to 100 m min\(^{-1}\) without any specific adjustment to the commercial printing press demonstrating the capability of large-scale functional printing.

After printing, we first use the sheet resistance (\(R_s\)) of the printed structures to evaluate the effect of GP addition on the conductivity of the commercial ink. Figure 2c shows sheet resistance values measured from ten randomly selected sheets of each print run. We note that the \(R_s\) values are high compared with screen printed samples. This is because of the differences in ink rheology requirements and maximum allowed pigment concentration in ink formulations for these print systems.\[^{[23]}\]

In addition, the high print speed in flexographic presses typically produces sub-\(\mu\)m thick printed structures, compared with \(\approx25\) \(\mu\m\) layers for screen printing.\[^{[9]}\] Further to this, our ink is not entirely graphene based. In this example, the pigment of the ink is solely graphene whereas we only use graphene as an additive to give rise to a cost-performance benefit. We find that the addition of GP to the commercial carbon-based ink reduces the \(R_s\) on both paper and PET. We propose that this reduction is due to the conductive GP flakes combining with the commercial carbon pigment particles, allowing the formation of more conductive pathways in the printed film.

The addition of GP reduces the \(R_s\) of the conductive inks, more so on PET than on paper. We suggest that the difference is due to the varying surface roughness (Paper: \(R_s = 0.45\) \(\mu\m\); PET \(R_s = 0.04\) \(\mu\m\)) and porosity of the paper substrate and lack thereof in PET. The absorption of carrier solvents by porous paper substrate instantly cause the conductive material to settle where they are deposited, as opposed to migration due to the capillary effects of evaporation, hence producing a more conductive network.\[^{[19]}\]

The printed pattern is designed with a set of touchpads and a connection point for a PCB microcontroller (Figure S4a, Supporting Information). As a demonstration device, we connect the printed pattern to a PCB microcontroller, battery pack and speaker which together form a capacitive touch sensor (Figure S4b, Supporting Information). The PCB is capacitively coupled to the print with either tape (on the top) or the substrate itself (from underneath) acting as the dielectric layer. When touched, the circuit is completed at the point of contact and triggers a sound from the speaker. Different touch-points are programmed to produce different sounds. Video S1, Supporting Information, demonstrates the operation of the device and fabrication of the R2R capacitive sensors. Although a simple demonstration, this suggests a fully scaled-up manufacturing method for low-cost printed electronics that can be useful for applications such as disposable sensors for IoT, smart packaging and enablers of next-generation technologies.

The quality of the prints can be evaluated and compared by studying line edge roughness (LER) arising from the random variations on the printed edges.\[^{[25]}\] We calculate the LER from the average of the absolute values of the profile deviations from the mean line (Figure 2f). This is measured across a random 100 \(\mu\m\) segment of the 0.1 mm line from the fiducial pattern (Figure S4a, Supporting Information, which represents the thinnest printed feature; Figure 2d,e). Upon incorporation of GP, we find that the LER reduces from 4.12 to 1.87 \(\mu\m\) on paper and from 4.93 to 3.98 \(\mu\m\) on PET. The small variations before and after the addition of GP are insignificant, and shows that the print quality is not adversely compromised with the enhancement with GP.

Uniformity in functional printing is paramount to the scalability as it allows for reproducible functional patterns in large-scale manufacturing. Printing uniformity can be evaluated in two
ways, the first is the intrasheet uniformity which allows performance reliability assessment of a printed device when multiple, related components (such as resistors) are printed. The second evaluation pathway is to probe the inter-sheet (i.e., sheet to sheet) uniformity, which indicates variations between different printed devices in a large-scale manufacturing set up. This ensures interface electronics can work with any and all of the printed sheets/devices. For conductive inks, $R_s$ is dependent on the composition and thickness of the printed layer, and therefore can be used as a sensitive indicator to evaluate uniformity of the printed samples. To investigate the intrasheet uniformity, we take 25 $R_s$ measurements across the functional area from randomly selected single sheets. The grid pattern we use for this and a set of example heat maps from the measurements are shown in Figure S5, Supporting Information. We maintain the relative positions in the sheet and present the heat maps as a visual representation of typical spatial changes in $R_s$ across the single sheets. From the maps, it is clear that there are small variations within each sheet. Such a level of variation is expected for printed samples due to minute but dynamic changes in variables such as roller-pressure and substrate tension under the high-speed R2R process. Multiple other factors may also play a part in print uniformity. These include temperature and varying viscosity of the ink due to solvent evaporation during the print run.\[30\]

To quantitatively assess the intrasheet uniformity, we then measure 25 data points on 25 randomly selected sheets from each of the four sample types across the print run. On Figure 3a, each point on the graph therefore corresponds to the average of the 25 measurements taken on that individual sheet, with the error bars indicating the corresponding intrasheet variability. The average of the intrasheet variability across the 25 sheets gives a greater insight into the uniformity of the individual printed sheets across the print run. For the paper substrate, the average intrasheet variability marginally reduces from 1.75 to 1.43 kΩ□⁻¹ upon GP-enhancement while on PET it reduces from 2.27 to 1.31 kΩ□⁻¹. This indicates that the addition of GP facilitates more uniform printed patterns. We propose that the improvement in uniformity is due to the larger lateral size of the GP compared with the commercial conductive carbon pigment particles, which promote a planar, more consistent conductive network across the printed patterns. The GP-enhanced ink on PET produced the most consistent print across individual sheets which we attribute to the lower surface roughness of the PET ($R_a = 0.04 \mu m$ compared with $R_a = 0.45 \mu m$ for paper). The SEM images in Figure S6, Supporting Information, show the difference in the bare surface of both substrates. We believe the lower, more consistent $R_s$ on PET is a result of the smoother surface, reducing the topological inconsistencies in the printed pattern.

**Figure 3.** a) Scatter plots with each point showing the intrasheet uniformity of sheet resistance across 25 individual sheets printed on both substrates with both inks, plotted in ascending order. b) Box plots generated from 625 measured points across each sample showing the spread of the data giving insight into the intersheet uniformity. The stars represent the mean average of all the points, the inverted triangles enclose 1–99% of all the data points. c) Histograms of the data plotted with normal distribution curves of the sheet resistance measured for each of the four samples.
We next analyze the 625 data points for each sample type to build a greater understanding of the intersheet uniformity across the individual print runs. The data are presented in box-plots; Figure 3c, which upon comparison on each substrate, shows that the respective $R_s$ values for GP-enhanced prints are reduced, representing a consistently better conductivity across the print runs. This is further elucidated in the histograms in Figure 3d, which show the distribution of the data points on each sample. From the graphs, we see lower $R_s$ values and narrower distributions for the GP-enhanced samples, illustrated by reduction in $\sigma$ from 2.08 to 1.80 for paper and 2.55–1.40 for PET. These $\sigma$ values correspond to a percentage variation from the mean $R_s$ of between $\pm 7\%$ and $\pm 12\%$ for all four samples. This comparatively narrow spread in $R_s$ is well within the level tolerated in manufacturing of printed thin-film transistors where from $\pm 10\%$ to up to $\pm 30\%$ variation in threshold voltage is acceptable.\(^{[33]}\) The validity of our data to represent the entire print run is also proven, as each data set takes on a normal distribution that is in line with the central limit theorem. We can therefore confidently assume that these results can be generalised across the entire print run. This shows the capability of flexographic printing to fabricate consistently performing 2D-material-based circuits on an industrial scale, laying the foundation for large-scale additive manufacturing.

Another key assessment aspect of functional printing is the adhesion of the printed structure to the substrate. This is indicative of the durability of the pattern and also the lifetime of any printed device. Adhesion can be tested by conducting various stress tests,\(^{[34]}\) common in the print/coating industry.\(^{[24]}\) We first conduct a tape test, which works by the application of a specific tape on the print, followed by its subsequent removal. Figure 4a shows the scanned images obtained during different steps of the tape test on each sample. On all of the samples, it is clear that a complete layer is removed from the original print, as shown by the residues on the tape. The GP-enhanced prints show a more uniform residue on the tape. This supports the previous observation that the GP-enhancement increases the uniformity of the print. The GP-enhanced samples also show a darker residue, indicating more materials are removed. We argue that the increase in pigment concentration (2.5 wt%) through the incorporation of graphene is too low to have an effect in the increased residues. Instead, we propose that the presence of more material on the tape from GP-enhanced samples is likely due to the stronger network formation by the graphene flakes. Figure 4b shows the change in $R_s$ as a result of the tape test. As expected, the $R_s$ for all samples increase after the tape test, as a result of the disruption to the conductive networks caused by delamination of part of the printed structure. The effect of the tape test is much less
pronounced in the GP-enhanced samples, again indicating their greater structural integrity compared with carbon-based inks.

To quantify and compare the adhesion of the GP-enhanced samples to both substrates, we use the American Society of Testing and Materials (ASTM) D3359 cross-hatch tape test. It is conducted by using a tool to score a right angle lattice pattern into the print penetrating to the substrate. A specific tape is then applied and subsequently removed. The remaining print is evaluated using the ASTM chart which gives a qualification of materials from 0B (very poor) to 5B (perfect, nothing removed). Figure 3c shows the microscope images before and after the tape application/removal. From these images, it is apparent that the adhesion on paper is worse, illustrated by greater amount of exposed areas close to the lines due to flaking of the print. This is attributed to the fibrous nature of paper which is more likely to be affected by the cross-hatching process. However, a closer look at the PET sample after tape shows more exposed areas in portions of the sample further away from the lines. To quantify the changes caused by the different stages of the cross-hatch test, image analysis of the microscope images was conducted using ImageJ analysis (Figure 4c). Figure 4d shows the loss of coverage from the original print, after scoring the sample with a standard cross-hatching tool and after the tape application/removal portion of the test as laid out in ASTM D3359.

It shows that a greater amount of the substrate was exposed on the print on paper than on PET. The coverage loss on paper after the tape portion of the test increases by 5%, and on PET it increases by 3.9%. Both fall under the 4B classification on the ASTM chart, which is the first level below “Perfect” for the adhesion test. This shows that the commercial scale functional flexographic printing is capable of manufacturing robust functional prints on both paper and PET.

Another way to probe adhesion, as well as the durability of a functional print on a flexible substrate is to conduct a cyclic bending test. It is an important test which gives insight into the lifetime of a printed device on a flexible substrate. The test involves repetitive bending of the printed pattern to a certain bend radius and observing the print before and after, also in real time to determine the effects of the bending on the printed material. We conduct a 1000 bend test on the GP-enhanced samples, collecting real-time resistance data throughout and observing the printed film at a central location on each sample before and after the test using SEM.

We conduct the bend test using an automated system which involves movement along a single axis to induce the bend in the sample. Figure 5a shows the sample in the bent (central bending radius = 3.1 mm, radius at joints = 5.1 mm) and the flat state. When a conductive, continuous thin-film sample is bent, small defects such as microcracks could develop across the bending direction and increase the resistance between the two points of contact. As long as the sample does not break or deform significantly, the resistance value typically returns to the original

![Figure 5](image-url)
level. Therefore, the stability of the resistance values during, as well before and after the bend test can be used as a qualitative metric to determine the durability of the printed film. We present our real time resistance data in Figure 5b,c. The resistance values in the flat state increase during the first few bends as a result of the microcracks that begin to irreversibly form with each subsequent bend. After this, the flat- and bent-state resistance values during the bend cycles stabilise and both samples show good durability across the bend cycles. The average resistance values of the first 100 bends in the flat state increase by 4.63% and 0.31% on paper and PET respectively when compared with the average resistance value over the last 100 bends. It is clear the GP-enhanced ink on PET sample is more consistent and more durable when compared with the GP-enhanced ink on paper sample. This is illustrated by the smaller difference in the average resistance of the first 100 bends and the last 100 bends (bent and flat) on PET and also the generally smaller standard deviation seen between the same data set for each sample. To try and understand the root of this, we take a closer look at the morphology of the surface of the printed patterns.

We analyze the changes in the surface morphology of the printed GP-enhanced films on both paper and PET by conducting SEM analysis of the sample before and after the bend test. In Figure 5d, we see representative images of the printed surface on paper before and after the bend test. There are clear cracks that have formed on the surface as a result of the bending of the sample. We do not observe any cracks of similar magnitude during the SEM characterization of the sample printed on to PET; representative images shown in Figure 5e. We attribute the difference in the cracking of the surface of the printed film to the thickness and surface of the substrate it is on (Figure S6, Supporting Information). The greater thickness of the paper substrate (74 μm) in comparison to PET (0.50 μm) naturally leads to a greater exerted tensile strain on the printed film on paper. We also propose that the rougher surface of paper contributes to the greater stresses on the printed film, leading to the formation of the cracks. The lack of such cracks shows the greater durability of the printed film on PET. We believe that due to the fibrous nature of paper, it is more prone to buckling, which contributes to a reduced durability of any printed pattern on the surface. We additionally note that there is no delamination of the print on either substrate as a result of the 1000 bend test, corroborating the good adhesion of the ink to either substrate.

The relatively consistent resistance change observed on both substrates between the flat and bent position after the initial crack formation is a key indicator of a long lifetime of the printed patterns on both substrates. This property presents the possibility of such printed patterns to be used as strain gauges. To show the applicability of the printed patterns for strain sensing, we calculate the average \( \Delta R / R_0 \), where \( R_0 \) is the resistance value in the flat state and \( \Delta R \) is the resistance in the bent state minus \( R_0 \), over the first and last 100 bends. The print on paper exhibits an average \( \Delta R / R_0 \) of 43.6% in the first 100 bends and 48.8% for the last 100 bends. On PET, the average \( \Delta R / R_0 \) is 63.8% and 65.4% for the first and last 100 bends, respectively. These \( \Delta R / R_0 \) values show promise for strain sensing\(^{16}\) and could be further optimised through ink composition. Though we have not calculated the amount of strain applied, the moderately consistent \( \Delta R / R_0 \) values measured over the first and last 100 bends shows potential for low-cost, large-scale fabrication of durable flexographically printed strain sensors on both paper and PET. This is just one of many other potential applications that could be scaled up to a commercial level by utilizing flexographic printing to produce robust functionalised prints on low-cost flexible substrates.

3. Conclusion

The maturity and scalability of printing processes make them appealing for large-scale manufacturing of printed electronics. In recent years, methods for incorporating functional nanomaterials into the liquid phase have developed significantly. The main challenge is now to formulate inks that are optimised for specific printing technologies. Among the different techniques available, flexographic printing has remained under-represented for functional printing, especially at large scale. This is likely due to a number of factors such as higher initial capital costs, complexity of the ink formulation, printer set up times, and availability required to achieve consistent printing compared with screen printing technology. Our work here is the first to demonstrate commercial scale, high-speed flexographic printing of graphene-enhanced inks on both paper and PET substrates.

The analysis we present in this paper based on a large number of measurements across the print run highlight four key aspects. First, commercial-scale flexographic printing is capable of producing largely consistent and uniform prints across large print runs at very high speeds, where GP incorporation increases the uniformity of the printed patterns. Second, as verified by the widely used tape and cross-hatch tests, GP incorporation promotes adhesion and better retention of the conductive patterns on both paper and PET. Third, the GP-enhanced prints exhibit good durability as corroborated by our results from the 1000 cyclic bend test. Fourth, the incorporation of GP affords advantages in conductive ink formulation, with only modest (3%) increase in cost. The conductivity is improved and the printed patterns become more uniform within individual printed structures and between printed sheets, considerably below the accepted threshold for statistical variation for large-scale manufacturing. This all together demonstrates that the incorporation of GP has multifaceted benefits while maintaining the ability to be printed at high speeds in an industrial graphics printing press with no modifications to the printer.

We finally note that printing can be utilized in sequential R2R systems in a single press and different materials can be incorporated with additional passes. For example, with further refinement, a single flexographic printing press could be used to print multiple materials using sequential rollers, similar to how they are used to print composite colors in the graphics industry. Flexographic printing can therefore be utilized to fabricate more complex and multilayer devices on an industrial scale. We hope that our demonstration of achievable uniformity under high-speed flexographic printing will lay the foundation for reliable and large-area volume manufacturing of 2D material-based multilayer printed devices.
4. Experimental Section

Ink Formulation: We used a commercial conductive carbon-based ink formulated by Novalia Ltd. for flexographic printing as received for the 0 wt% GP samples. A three-roll mill was used to achieve a uniform dispersion of the carbon pigment in the ink.[4,9,10] The three-roll mill consisted of a feed roll, a center roll, and an apron roll that rotate in opposing directions at differing speeds. It served as a dispersion method by employing the high shear forces generated from the motion of the rollers to break down the aggregates into primary particles.

We used graphene powder from Perpetus Advanced Materials (NGP03) to enhance this ink. We added 25 wt% of the powder to a ternary solvent mixture of ethanol:ethylene glycol:water with a ratio of 65:30:5 (by mass) and subjected it to sonication for 30 min and then stirring for a further 12 h, forming a stable dispersion. Hundred grams of this dispersion was added to 900 g of the commercial ink to make 1 kg of the ink, with final graphene loading of 2.5 wt%. The mixture was then processed using a Silverson LS5m laboratory high-shear stator-rotor mill at 4000 rpm for 1 h. The jar was kept in a water bath to dissipate the heat generated. This ink was again processed through a three-roll mill before it was used on the printing press.

Raman Spectroscopy: We conducted Raman measurements using a Renishaw inVia micro-Raman spectrometer, using an Ar laser (λ = 514.5 nm) at a laser power of 0.1 mW and an acquisition time of 10 s.

Ink Rheology: We used a parallel plate rheometer (DHR Rheometer from TA Instruments) to measure the rheological properties of the ink. The ink was placed across the print, then removed it. The adhesion was evaluated by analysis of optical microscopy images of the sample before and after the tape test, and comparing the images reported by ASTM.[35] We used ImageJ processing software to analyze the microscope images obtained to determine coverage.

Cyclic Bending Test: We carried out a 1000 bend test by cutting out strips of GP-enhanced printed samples on paper and PET. We further cut the samples in half. The first half was used to characterize the sample before the bend test, and the other was subjected to 1000 bending cycles using an automated bending set up, and then characterized.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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printing, 2D materials, flexographic printing, roll-to-roll, functional ink, graphene

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