Flexible and Stretchable Temperature Sensors Fabricated Using Solution-Processable Conductive Polymer Composites

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1. Introduction

Temperature, a fundamental physical parameter, varies spatially and temporally. Accurate measurement of localized temperature on biological tissues—even while undergoing deformation or dynamic movement—would be useful in disease diagnosis and monitoring. Distinguishing signals from the surface of skin without impeding the users’ movement or measuring temperature on a curved surface such as a forehead is unachievable in traditional, rigid contact sensing devices. While infrared (IR) devices and thermal imaging cameras can provide fast results, a line of sight with the object must be maintained, and knowledge of the emissive properties of the surface are required. To monitor dynamic and spatial variations in temperature, many approaches have been reported on the development of flexible and stretchable sensors. One approach is to pattern temperature responsive materials on sheet-like flexible substrates. Responsive elements are comprised of metals (e.g., platinum, nickel, gold, copper) that exhibit a linear increase in resistance as a function of temperature. This change in resistance results from the fact that as temperature increases, so do the number of collisions/scattering events between electrons and phonons.

This behavior can be described numerically by the temperature coefficient of resistance (TCR), which is defined as the relative change in resistance per degree Celsius change in temperature. Typical TCR values for metals fall in the range of 0.003–0.006 °C⁻¹, where higher values correspond to higher sensitivity. Substrate properties are also important; in addition to providing mechanical stability and flexibility, the total thermal mass of the device must be small to avoid interfering with measurements. Thin polymer sheets or films are therefore often used, including polyimide, elastomers, polyethylene terephthalate (PET), and fabrics. For example, Rogers and coworkers designed platinum (Pt) patterns on the surface of Kapton (polyimide) tape with a measurable range of 20–100 °C. This Pt sensor is flexible, highly accurate, and resistant to oxidation though Pt is quite expensive and difficult to process. An alternative metal is nickel (Ni), which has the highest known TCR among metals (0.006 °C⁻¹), and—it like Pt—is processed using the standard microfabrication techniques of sputtering and lithography.

Recently, electrically conductive polymer composites (CPCs) have been implemented as stimuli-response materials that undergo a measurable change in electrical properties (e.g.,
resistance, capacitance) upon exposure to the stimulus of interest. In these composites systems, conducting nanoparticles (e.g., carbon-based materials or metal particles) impart electrical conductivity to the composite, while the polymer matrix (which is typically insulating) provides mechanical stability. At low concentration the composite may be non-conductive, however when the loading of nanomaterials is increased beyond a certain threshold the resistance may drop abruptly. The particular filler content at which this change occurs is called the electrical percolation threshold. One advantageous property of CPCs is that they are compatible with printing techniques including direct ink writing (DIW), 3D printing, and screen-printing, and may therefore be patterned without the use of photolithography.

In a CPC, either the polymer or nanofiller (or a combination thereof) may act as the sensing element that responds to changes in temperature. For example, the polymer may expand upon heating, increasing the separation between the conductive particles, leading to an increase in resistance (indicating that the material has a positive temperature coefficient, PTC). If the material composition is initially near the percolation threshold, the resistance can increase by several orders of magnitude upon heating. Thus PTC-type temperature sensors have been intensively used in overheat protection and self-controlled heating. The responsibility of a CPC may also result from the temperature-dependent properties of the nanofiller, some of which undergo a decrease in resistivity as a function of temperature (corresponding to a negative temperature coefficient [NTC]). However, even if the filler undergoes a decrease in resistivity as temperature increases, the composite itself may have a PTC overall due to the thermal expansion of the polymer. These competing effects can result in low or non-linear temperature-dependent electrical behavior. To address these problems, one approach is to add large-aspect ratio fillers, which could create more electrical contacts, minimizing the effect brought from volume expansion under heating. For instance, Chu et al. compared the sensing performance of low and high aspect ratio carbon nanotube/CNT)/polydimethylsiloxane (PDMS) composites and found that composites formed with high aspect ratio CNTs underwent larger drops in resistance upon heating than composites formed with low aspect ratio CNTs; the authors hypothesized that the longer (higher aspect ratio) CNTs were able to maintain a more connected network upon thermal expansion of the PDMS than the shorter (lower aspect ratio) CNTs. In 2018, an NTC material was engineered by forming a foam of a CPC (carbon black/chlorinated poly(propylene carbonate)). When this porous material was heated, the expansion of the gas trapped in the pores resulted in the compression of the walls, causing a reversible increase in conductivity (as measured from 20 to 70 °C). However, the behavior of the material under mechanical deformation was not studied. Overall, very few polymer NTC materials with favorable sensing performance near body temperature have been illustrated.

Reduced graphene oxide (rGO)—a grapheneic material synthesized by thermal or chemical reduction of exfoliated graphene oxide (GO)—has been used in composites due to its large surface area and favorable electrical properties (relatively good electrical conductivity, high charge carrier mobility, and large carrier density). Pressed powders of rGO have a NTC, as the number of charge carriers increases with temperature, resulting in a reduction in resistance. However, these sheets tend to be very brittle and delicate, and therefore are not desirable for use in deformable sensors. Furthermore, a variety of chemical sensors have been implemented that leverage the change in conductivity that occurs when a gaseous analyte (such as water vapor) interacts with the surface of rGO, suggesting that rGO-based sensors may not have good selectivity for temperature. The mechanical properties of rGO can be improved through the formation of a composite; likewise, embedding rGO in a polymer with limited permeability could reduce interference from undesired analytes such as water vapor. For example, Lee et al. reported a gated rGO/polyurethane composite temperature sensor fabricated using standard lithographic techniques. Their sensor array showed up to 0.001/sensitivity, and can be mounted on skin to monitor human temperature. However the sensor is sensitive to mechanical deformation, costly due to the complexity of lithographic fabrication, and exhibits relatively low sensitivity.

To engineer a highly responsive CPC based on rGO, the properties of the matrix must be carefully selected. A small thermal expansion coefficient is key to ensuring that the response of the material is dominated by the temperature-dependent properties of the rGO rather than by the thermal expansion of the polymer. In this work, we engineer rGO polymer composites for use in wearable temperature sensors utilizing a polymer matrix with low thermal expansion, high thermal stability, and good resistance to moisture: polyhydroxybutyrate (PHB). PHB is a biopolymer produced by bacteria that is biocompatible. The thermal expansion coefficient of PHB (40 µm mK⁻¹) is relatively low compared to polyester (125 µm mK⁻¹), polyethylene (PE) (200 µm mK⁻¹), and PET (59.4 µm mK⁻¹). PHB has a high melting temperature (175 °C), which should enable stability over a wide range of temperatures. PHB is also highly hydrophobic, which should make PHB-based devices and composites resistant to water. Finally, PHB is soluble in chloroform and boiling acetic acid, enabling solutions to be formed that can be patterned using various printing techniques. In our previous work we compared the chemical and physical properties of PHB/rGO composites prepared using three different reducing agents, and found that—at room temperature—composites prepared using L-ascorbic acid by an in situ reduction method demonstrated very low percolation thresholds (0.1 vol%) and with relatively high conductivity at 8% loading. The excellent dispersion of these materials was shown using x-ray diffraction (XRD).

In this work, we investigate the suitability of a solution-processable polymer-reduced graphene oxide composite as a temperature-sensing material, and then manufacture and characterize printed devices incorporating this material. The responsive composite is formed from PHB matrix and sheet-like nanofiller (reduced graphene oxide [rGO]) with large lateral dimensions (40–50 µm). These composites are non-toxic and solution-processable. We first examine the temperature-dependent electrical properties of the CPCs, for comparison against neat rGO. The physical, electrical, and mechanical properties of composites with rGO loadings of 3 to 12 wt% are systematically investigated. To explore the percolation behavior of the materials, in addition to the typical characterization of conductivity, both the mobility and charge carrier density of the samples at various filler loading are measured. To demonstrate...
the manufacturability of the materials, temperature-sensing devices are fabricated by drop-casting rGO-PHB solutions on the surface of inkjet-printed silver electrodes, and the temperature response, durability, stability, and water-resistance of the devices are characterized. An array of devices (6 × 7, 12 × 12) are printed on a flexible substrate, and used to map the temperature profile of an object. To demonstrate that the PHB/rGO composites can be used in mechanically flexible temperature sensors, both thin, stretchable elastomeric substrates and functional meandering composite lines are printed by DIW. High adhesion is achieved between the active layer and the substrate, and the resulting devices can withstand strain while undergoing only a small change in resistance. As a proof-of-concept, the printed devices are then used to monitor temperature on the surface of skin.

2. Materials

PHB biopellets were purchased from Bulk Reef Supply, USA. The molecular weight was determined by gel permeation chromatography (GPC) to be $M_w$: 190 kDa. The GPC method is described in our previous work.[51] Large scale graphite flakes were purchased from Alfa Aesar Inc. Sulfuric acid (98%), hydrogen peroxide (30%), phosphoric acid (98%), hydrochloric acid (37%), and potassium permanganate particles were purchased from Fisher Scientific, Canada and used as received. Glacial acetic acid (99%), L-ascorbic acid (l-A.A) were provided from Sigma-Aldrich, Canada, and used as received. Silver ink was purchased from AgIC Inc, Japan and poured directly into the cartridge for inkjet printing. PET film (Melinex 516, 3 mil) and silver paste (Pelco silver paste [Ted Pella, Inc.]) were used as received. Polydimethylsiloxane (Sylgard 184, Dow Corning) was purchased from Sigma-Aldrich and was mixed in the standard 10:1 ratio of elastomer: crosslinker prior to use.

3. Experimental Section

3.1. Preparation of GO Slurry

To synthesize graphene oxide (GO), graphite sheets with large lateral size were oxidized using the improved Hummer’s method.[52] In detail, sulfuric acid (360 mL)/phosphoric acid (40 mL) was mixed with 3 g of graphite. 18 g of potassium permanganate, an oxidizer, was then added drop-wise into the above mixture under continuous stirring with constant maintaining temperature of 45 °C for 16 h. The mixture was then allowed to cool to the room temperature before pouring the dispersion over 400 g of ice to quench the reaction. Hydrogen peroxide was slowly added drop-wise to the chilled solution until the dispersion turned a whitish yellow color. The slurry was separated from the acid by centrifugation and then resuspended in water. The resulting GO was washed twice with hydrochloric acid and followed by three washes with ethanol and then kept in beaker for use.

3.2. Preparation of rGO/PHB Composite Ink

The composite rGO/PHB ink was prepared using an in situ reduction method described in a previous work by the authors, as illustrated in Figure 1.[48] In detail, a solvent exchange was performed to transfer aqueous GO slurry to acetic acid by centrifuging the slurry at 20 000 rpm for 10 min and then replacing the solution with acetic acid (twice), ultimately forming a solution with a concentration of 1 mg mL$^{-1}$. The mixture was brought to a boil, and roughly 0.04 g of PHB pellets was added to act as a stabilizer; l-A.A was then added to the suspension (2:1 weight ratio, l-A.A:GO) under vigorous stirring and continuous heating at 118 °C for 2 h. No purification step was needed to remove the l-A.A. The desired proportion of PHB was dissolved in A.A solution to form a homogeneous mixture at 118 °C. The resulted black suspension was cooled to room temperature and kept in beaker for further use with no visible agglomeration. To fabricate temperature sensors, the composite ink was shaken well and a drop was dispensed onto the printed electrodes on a 140 °C hotplate. Substrate heating continued until all the solvent was evaporated (when the ink formed a visibly shiny and smooth surface, typically around 1 min).

To convert the weight fraction to volume fraction, both density of rGO and PHB were used, with a value of 2.2 g cm$^{-3}$ and 1.25 g cm$^{-3}$, respectively. These values were input into the following equation: $\text{vol} \% = \frac{\rho_{PHB} \cdot A + \rho_{rGO} \cdot B}{\rho_{PHB} + \rho_{rGO}} \times 100\%$, where $\rho$ is the mass (g) of the PHB matrix (0.5 g). For example, 3 wt% rGO loading equals to 1.74 vol% loading.

3.3. Preparation of Compressed rGO Powder

GO was reduced by l-ascorbic acid using the same method as for the composite preparation except that PHB was not added to the acetic acid solution. In detail, the centrifuged GO (20 000 rpm, 10 min) was dispersed in A.A solution with a concentration of 1 mg mL$^{-1}$. The mixture was stirred continuously (200 rpm min$^{-1}$) on hot plate at the boiling point of A.A. Then, the ascorbic acid (l-A.A) was added to the mixture with the weight ratio of 2:1 to GO, and the reduction process proceeded for 2 h under boiling. The resulting black suspension was washed by water three times and then dried in an oven (80 °C) overnight. The dried powder was compressed into films on hot compressor at a pressure of 25 GPa without heating.

3.4. Preparation of Silver Electrodes for Ag/Drop-Coated Composite Devices

The branched electrodes were designed with the software SketchUp and printed using an office printer (Epson 2700) on glossy PET paper. No heat treatment was needed for the silver electrodes. Conductive composite dispersions (at room temperature) could then be drop-coated on the traces and allowed to dry to form the Ag/drop-coated composite devices shown in Figure 1.

3.5. Direct Ink Writing of PDMS Substrates and Conductive Composites

An ink extrusion system was built using a dual syringe pump (Harvard Apparatus, Pico Plus Elite) and a fused deposition
modeling (FDM) printer (Geeetech, China) capable of moving in x-, y-, z-directions. A 5 mL syringe was loaded on the syringe pump, and was connected via flexible silicone tubing to a needle that was mounted alongside the nozzle of the FDM printer. The setup is shown in Figure S1, Supporting Information. To print a thin PDMS substrate, 10 g of Sylgard 184 base and 1 g of crosslinker were mixed for 5 min and allowed to sit for 30 min to remove air bubbles before loading to the 5 mL syringe with a 750 µm nozzle output, and the syringe pump rate and nozzle speed was set at 20 mL h$^{-1}$ and 1000 mm min$^{-1}$, respectively. PDMS was first printed on top of Kapton; the hot stage of the 3D printer (beneath the sample) was then heated to 100 °C for 5 min to partially cure the PDMS. Prior to curing PDMS is a viscous fluid, so both a thin printing layer and high curing temperature are necessary. The resulting thickness of a typical layer of PDMS was 30–40 µm. For DIW, a conductive ink suspension was prepared by dissolving around 0.5 g PHB and the desired proportion of rGO in 10 mL of boiling acetic acid for around 30 min. The ink was then cooled to room temperature and loaded into a 5 mL syringe with a 23 G (about 330 µm) needle. The conductive designs were extruded at a speed of 80 mL h$^{-1}$ using syringe pump, with a needle moving speed was set at 3200 mm min$^{-1}$. A typical printed composite trace is around 10 µm thick.

3.6. Characterization

3.6.1. Morphology

A Zeiss Sigma 300 VP field emission scanning electron microscope (FE-SEM, Cambridge, UK) was used to observe the cross-sectional images of samples. A thin layer of gold (10 nm) was deposited onto the sample by using Denton sputter (DV1S)/24LL, Denton Vacuum, USA) to avoid surface charging during SEM observation. The images were collected using the secondary electron (SE) mode with a voltage of 3 kV. Cross-sectional images were obtained by fracture frozen samples under liquid nitrogen for SEM imaging. To prepare samples for optical microscope, composites were microtomed to slices 200 µm thick and mounted on glass slides. A Celestron 400x optical microscope (Laboratory Biological Microscope Inc., Canada) was used to investigate the microtomed surfaces. To prepare samples for transmission electron microscopy (TEM), 1 wt% composites were microtomed to slices 200 nm thick and mounted on glass slides before imaging. A Philips EM301 electron microscope (Philips Electronic; Mt. Vernon, New York) was used for TEM imaging and was operating at 80 kV.

Figure 1. PHB and reduced graphene oxide (rGO) composites synthesis fabrication of devices consisting of printed Ag electrodes with drop-coated rGO-PHB composite sensing elements (µm thickness).
3.6.2. Resistance Measurements

The resistance of patterned sensors was measured as a function of temperature using a homemade setup. A Peltier thermoelectric stage (Adcol, China) with voltage supply source was used as a heating source. The temperature was varied from −10 to 100 °C, at heating rate of roughly 1 °C min⁻¹. Samples were mounted on the center area of the Peltier stage and loosely covered by cotton pads to avoid heat loss. The samples were connected by Al wires to a source meter (Keithley 2401, USA), which supplied a voltage of 1 V; the resistance of each individual sensor was recorded serially as the temperature was varied.

3.6.3. Conductivity and Mobility Measurements

The in-plane conductivity, mobility, charge carrier density, and Hall voltage of both pressed rGO powder and composite films were determined by ACCENT HL5500 Hall System at room temperature using the van der Pauw method. Films were prepared with a thickness of 80 µm and cut into 7 mm × 7 mm squares. The drop-cast sensing area had a diameter of around 1 cm, and thickness of 80 µm. The direct-ink-printed composite ink lines had a typical thickness of 10 µm. Contacts were defined at each of the four corners of the sample using a layer of silver paste followed by aluminum electrodes to which wires were connected. Photographs of the mobility measurement setup and sample configuration are shown in Figure S4, Supporting Information. During measurement, a magnetic field (0.325 T) was applied perpendicular to the plane of the film, and current (0.1 µA for highly resistive materials to 0.1 mA for less resistive materials) was applied between two of the electrodes at opposite corners while the voltage was measured between the remaining two electrodes.

3.6.4. Temperature Measurements

Characterization of Arrays: Printed silver connections were individually probed with flat copper probes connected to a Keithley 2401 source meter. Resistance data was recorded automatically using Kickstart software. Temperature measurements on skin: Devices were connected to thin copper wires by silver paste. Sensors were placed on the surface of the forehead or wrist as data was collected using Keithley 2401 source meter and Kickstart software. Permission was obtained from the subject; ethics approval was not required from the institution for proof-of-concept demonstration of the devices.

3.6.5. Mechanical Properties

An Instron 5943 tensile tester (Instron, Norwood, MA, USA) equipped with a 1 kN load cell was used to investigate the mechanical properties. Compressions tests were performed on all devices to test the cyclability. Samples were fixed on the center of compression flatten, and rod with a flat, circular end (diameter 10 mm) was clamped with the top set of clamps to apply a load. A constant load of 40 kPa was applied at a rate of 0.5 mm min⁻¹. Bending tests were performed by fixing one end of a sample to a stationary holder while using a linear motor to displace the other end. During compression and bending tests, electrodes were connected to the Keithley 2401 so that resistance data could be recorded.

3.6.6. Statistical Analysis

The sensitivity value were displayed as the mean stand ± standard deviation (SD). Sample number were for n ≥ 3 per group. Statistical calculations were utilized by one-way analysis of variance (ANOVA), followed by student’s t-test was utilized to determine the statistical significance of resistivity data for each type composites. Results were determined to be statistically significant (p < 0.05, Figure S10, Supporting Information).

4. Results and Discussion

4.1. Morphology of rGO/PHB Composites

To investigate the cross-sectional morphologies of plain PHB and composites, samples were imaged using both scanning electron microscopy and transmission electron microscopy, and the results were shown in Figure 2. For neat PHB and samples with lower concentrations of rGO (1 wt% and 2 wt%), relatively homogeneous fracture surfaces were observed by SEM. However, at these low concentration values, rGO was difficult to observe in the SEM images. At higher concentrations of rGO (3 wt% and above) the fractured surface appeared increasingly brittle, and the rGO flakes (indicated by dashed squares) were visible and appeared randomly distributed in the matrix. The observed change in the brittleness of the fractured surface suggests that the presence of the rGO impedes the deformation of the polymer under elongation. The optical images of micrometed surfaces of the composites are shown in Figure S2, Supporting Information, and these images indicated a similar trend as the SEM images, where rGO sheets were randomly distributed through the PHB matrix with no visible large agglomerations of filler. These results confirmed that the rGO was well distributed in the polymer matrix.

To better observe the dispersion of rGO inside PHB matrix, TEM was used to image a 1 wt% composite sample that was micrometed to 200 nm in thickness. In Figure 2g, fairly uniformly distributed wrinkles (dark gray in color) are visible in the polymer matrix (light gray). At higher magnification (Figure 2h), the wrinkles appear to be rGO sheets. Overall, a relatively good rGO dispersion was achieved in the composite material, although some rGO agglomeration can be seen.

4.2. Electrical Testing

The resistivity of a neat, hard-pressed film of rGO powder was investigated as the sample was heated from 20 °C to 70 °C (Figure S3, Supporting Information). As shown in Figure 3, the normalized resistivity (R0 − R)/R0 underwent a decrease as a function of temperature, indicating that the material has a NTC.
A non-linear relationship was observed, which is consistent with previous measurements in the literature, which have been shown to follow an Arrhenius-like dependence on temperature, consistent with a model in which the bandgap of the rGO dominates the temperature-dependent charge transport behavior\cite{53,54}. The TCR over the range of measurement was calculated to be $-0.0184 \, ^\circ C^{-1}$ from 20 to 60 $^\circ C$, the absolute value of which is much higher than for Nickel ($0.006 \, ^\circ C^{-1}$), indicating that the material is quite sensitive to temperature. These results suggested that rGO material is capable of making a good temperature sensor.

To investigate the mechanism of charge transfer in the materials, the temperature-dependent $I$-$V$ characteristics of both neat, compressed rGO powder and 3 wt% composite were characterized from 20 to 70 $^\circ C$ (Figure 4). As the voltage was swept from $-5$ to $+5 \, V$, a linear and symmetric response was observed for both types of samples. This linear relationship indicates that both the compressed rGO powder and rGO-PHB composites exhibited
Figure 5. a) Conductivity versus volume fraction of the composites at room temperature; the inset graph is the fitting curve used to calculate the critical exponent ($t$). b,c) Mobility and charge carrier density change as a function of rGO volume fraction, respectively.

The electrical conductivity of nanocomposites with different rGO concentration was measured by electrometer model 6517A (resistivity $>10^4 \, \Omega \cdot \text{cm}$), and four point probe method (Kelvin sensing), and the results are shown in Figure 5a. The conductivity of plain PHB was measured to be $10^{-15}$ S cm$^{-1}$ (indicating that it is highly insulating); composites with very low loading of rGO also exhibited very low conductivity. As the loading of rGO increased past 0.50 vol% (around 1 wt%), the conductivity rose sharply to $10^{-5}$ S cm$^{-1}$. This increase of 10 orders of magnitude can be explained using percolation theory: a fully conductive network forms when a threshold volume fraction is reached. This effect can be described by the electrical percolation theory equation, 

$$\sigma_c = \sigma_f [ (\varphi - \varphi_c) / (1 - \varphi_c) ]^t$$

where $\sigma_c$ is the intrinsic conductivity of nanofiller (here, rGO), $\varphi$ is the volume concentration of filler, $\varphi_c$ is the concentration of nanofiller at the percolation threshold, and $t$ is the critical exponent (calculated by fitting the curve). To report conductivity measurements, the mass fraction of each rGO concentration was converted to volume fraction based on the densities of PHB and rGO (as described in the Experimental Section). In our system, the measured percolation threshold was determined to be 0.50 vol% (around 1 wt%), which is a very low value among those reported for rGO-based nanocomposites. This is due to the large aspect ratio of the rGO achieved using our in situ reduction process of rGO, which resulted in a relatively high intrinsic conductivity ($10^2$ S cm$^{-1}$). A rapid increase in the plane electrical conductivity was observed as increasing the concentration of rGO filler (Figure 5a). The critical exponent $t$ was derived from linear fitting of the log $\sigma_c$ versus $(\varphi - \varphi_c) / (1 - \varphi_c)$ data (shown inset in Figure 5a), and was found to be $2.41 \pm 0.23$. For 3D networks, $t$ has been predicted to be between 1.65 and 2, while for 2D networks $t$ is expected to be 1.33. A larger $t$ suggests larger size of the clusters inside the polymer matrix. Values larger than 2 have been determined experimentally for conductive composites formed from materials such as multiwalled carbon nanotubes in poly(methyl methacrylate) ($t = 2.34 \pm 0.19$); solvent thermally reduced graphene oxide polyvinylidene fluoride ($t = 2.64$) and emulsion mixing of graphene and polycarbonate ($t = 4.18$). These different values of the critical exponent $t$ are dependent not only on the dimensionality of the filler but also on the physical characteristics—including size and orientation of the conductive filler.

The Hall mobility and charge carrier density of the composites were measured using the Van der Pauw method, and the results are shown in Figure 5b,c. The entire measuring system picture is in Figure S4, Supporting Information. As expected, the charge carriers were determined to be electrons based on the polarity of the measured voltage. These data showed that both mobility and number of carriers increased with increasing the rGO filler content, and significant changes in each of these properties occurred near the same vol% loading as for the changes in ohmic behavior at a given temperature. In addition, the higher current seen at a given voltage for a higher temperature indicated that the resistance of the sample decreased as the temperature increased, due either to a change in the number of charge carriers or a change in carrier mobility, or due to a synergistic combination of the two. No obvious lag or hysteresis was observed in any of the measurements, showing that fast response of composites to the external temperature change.
conductivity (±0.50 vol%). The Hall-effect measurements of the composites suggested that mobility and the number of carriers are highly influenced by the addition of the nanofiller. Both of these properties increased significantly above the percolation threshold (0.50 vol%) and increased steadily with the relative high loading of rGO filler in the polymer. The rGO mobility determined here (2100 ± 566 cm² V⁻¹ s⁻¹) is one order of magnitude higher than reported for other rGO. [43] This increase can be attributed to the effectiveness of our in-situ solution-based processing route. We found the charge carrier density can be broadly fit in the threshold equation: \( n_c = n_r \left( \frac{\bar{f} - \Phi_c}{1 - \Phi_c} \right) \), where \( n_r \) is the composite charge carrier density, \( n_r \) is the carrier density of nanofiller (here is the rGO, 10¹⁶ cm⁻²), where the rest of the parameters are the same as electrical threshold.

Below the electrical percolation threshold, both mobility (\(<10⁻³ \text{ cm}² \text{ V}⁻¹ \text{ s}⁻¹\)) and charge carrier density (\(<10⁹ \text{ cm}⁻²\)) were very low, thus resulting in high electrical resistivity (\(> \text{MΩ cm} \)). Once the filler content was close to the electrical threshold (e.g., 3 wt% or 0.05 vol% rGO), although the carrier density was still low, the mobility increased around four orders of magnitude to 1 cm² V⁻¹ s⁻¹; thereby increasing the overall conductivity.

As seen in Figure 4, increasing the temperature of either a pressed rGO powder or a 3 wt% rGO-polymer composites results in an increase in conductivity. As we were unable to perform Van der Pauw measurements at elevated temperatures, we were unable to directly determine whether this effect was due to an increase in the number of charge carriers or an increase in carrier mobility. However, in general, the mobility of the charge carriers is expected to decline as a function of temperature due to an increase in phonon scattering. [62] This suggested that there must be an increase in the number of carriers as the temperature increases.

The change in relative resistance as a function of temperature was explored for devices consisting of rGO-PHB composites of varying composition drop-coated on ink-jet-printed silver electrodes. Relative resistance was measured from room temperature to 70 °C, and the results are shown in Figure 6. Like the pure rGO sample, the resistance of all devices decreases with temperature, exhibiting a NTC effect. Overall, the curves are more linear than for the pressed rGO, although the overall magnitude of the response is smaller (Figure S5, Supporting Information, for comparison on a single plot). A large, linear response is desirable as it simplifies the interpretation of the data. Among these devices, those fabricated with the 3 wt% composite underwent the largest change in relative resistance upon heating (\(-0.008 °C⁻¹\)), with TCR values of \(-0.006 °C⁻¹\), \(-0.005 °C⁻¹\), \(-0.004 °C⁻¹\), \(-0.003 °C⁻¹\) for devices made using 6 wt%, 8 wt%, 10 wt%, and 12 wt% composites, respectively. The resistivity and calculated TCR values were summarized in Table 1.

The drop-coated device made using the 3 wt% composite, exhibited the highest absolute TCR value. The 3 wt% composite is the closest to the percolation threshold, which should make it most sensitive to variations in rGO loading: our results show that this sample is also the most sensitive to changes in temperature. Samples which are further below the threshold—such as 1 wt% and 2 wt% rGO-PHB composites—show high resistivity at room temperature, and this value changes little as temperature increases (data not shown). Similarly, samples with rGO content well above the percolation threshold (e.g., 10 wt% and 12 wt%) have relatively low resistivity at room temperature, and the resistivity of these composites varies little with temperature, despite the fact that the number of charge carriers in the rGO itself increases with temperature (as discussed above). This suggests that the mobility of the composite as a whole is more restricted at elevated temperatures at higher wt% rGO loadings than for lower wt% rGO loadings.

In terms of designing a sensor material with a large response, stable signal, and low power consumption, the neat rGO has the most desirable electrical properties: it has both the lowest resistivity and largest TCR value. However, this material is also known to be delicate. [63] and is prone to delamination and cracking when exposed to even small deformations. The mechanical stability of a pressed powder of rGO was briefly tested by a bending test, and, as can be seen in Figure S6, Supporting Information, this deformation caused the material to crack the first time that it was deformed. A typical 8 wt% drop-cast device under bending is also shown in Figure S6, Supporting Information. Like the other composites tested, the film is mechanically stable up to bending radii of 5 mm (i.e., shows no signs of cracking or delamination). The limited mechanical stability of the pressed rGO makes it unsuitable for use under deformation.

Drop-coated devices incorporating both neat rGO (without PHB) and composites films were also subjected to cyclic changes.

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**Table 1.** TCR and resistivity values for compressed rGO and different concentration composites.

| Material | TCR Value [°C⁻¹] | Resistivity [Ω cm] |
|----------|------------------|--------------------|
| rGO      | −0.018           | (1.1 ± 0.2) × 10⁻² |
| 3 wt% Composites | −0.008          | 80 ± 6.4           |
| 6 wt% Composites | −0.006          | 16.3 ± 1.8         |
| 8 wt% Composites | −0.005          | 5 ± 1.0            |
| 10 wt% Composites | −0.005         | 3.7 ± 0.2          |
| 12 wt% Composites | −0.003         | 1.1 ± 0.1          |
in temperature as their resistance was monitored and the results are shown in Figure 7. The devices were heated from room temperature to a peak temperature of 30 °C, kept at the peak temperature for 5 min, and then cooled back to the room temperature; similar heating cycles were subsequently applied to peak temperatures of 40 and 50 °C. During each heating cycle, the absolute relative resistance of each device increased; upon cooling the resistance of each device returned to its initial value. As in the previous characterization the devices constructed with pure rGO exhibited the highest response (largest change in relative resistance), followed by devices fabricated using 3, 6, 8, 10, and 12 wt% composites. For example, the sensitivity of rGO sample at 30 °C was almost double than the 8 wt% sample. The 3 wt% composite, which has filler content near percolation threshold, had the highest \((R_0 - R)/R_0\) among composites in each temperature step. Although 12 wt% had the lowest \((R_0 - R)/R_0\) values, the overall resistance measured from the instrument was quite stable with no obvious fluctuations (very narrow error bars). This is an important point considering for real applications.

Selectivity is an important characteristic of a sensor. To determine whether the materials are responsive to pressure and humidity, the resistivity of a set of rGO-PHB composite devices were characterized during cyclic compression, bending, and upon exposure to water. To fabricate functional devices, a responsive composite with high sensitivity (i.e., high TCR) and low resistivity (to achieve a more stable signal and to minimize ohmic heating during measurement) was desired. To balance these characteristics, the 6 wt% and 8 wt% composites were therefore selected for device fabrication and selectivity testing; as was summarized in Table 1, these material showed intermediate TCR values comparable to those of bulk nickel (−0.006 °C⁻¹ and −0.005 °C⁻¹, for the 6 wt% and 8 wt% materials, respectively. Nickel: 0.006 °C⁻¹), and also exhibited relatively low resistivity at room temperature (16.3 ± 1.0 Ω cm and 5 ± 1.0 Ω cm for the 6 wt% and 8 wt% materials, respectively).

The response of the 8 wt% composite to compression and bending are shown in Figure S7, Supporting Information. The relative resistance change over 1600 cycles of compression (loading and unloading test) (20 kPa), are shown in Figure S7a, Supporting Information, and the set up for the compression test is shown in Figure S7b, Supporting Information. Only a small change in relative resistance is observed, indicating that the device is relatively stable in compression. When the samples undergo bending, the relative resistance changes by up to 25% over an applied tensile strain of 3% (Figure S7c,d, Supporting Information). Similar results were observed for the 6 wt% samples, undergoing a change in relative resistance of up to 23% over an applied tensile strain of 3% (results not shown).
The resistivity of pressed rGO, 6 wt% and 8 wt% rGO-PHB devices were characterized upon exposure to water vapor (Figure S8, Supporting Information). While the relative resistivity of the composite remained fairly constant, the resistivity of the pressed rGO increased by over 100% as the relative humidity was varied from 20% to 90%. The relative resistivity of the composite film was further tested during immersion in water as the temperature was cycled from 20 °C to 80 °C (Figure S8b,c, Supporting Information). The results were highly repeatable, showing the stability of the measurements even upon immersion in water. Little difference was seen between samples measured in air and in water. Overall, these results suggest that the drop-cast film devices are almost inert to the external pressure, moisture and gave stable response over cyclic measurement, but are sensitive to the mechanical deformation (bending). This indicates that care should therefore be taken to calibrate and operate devices at a relatively fixed radius of curvature. Stretching was not investigated for any of these devices as the PET substrate is not itself able to undergo a significant elongation before break.}

For measuring spatial temperatures, a 6 × 7 array of devices using was printed on a PET substrate (Figure 8). The 8 wt% composite was selected for this application due to its low resistivity and acceptable TCR value. Each device consisted of a set of silver electrodes (Figure 8b) onto which the desired composite was deposited. To demonstrate spatial mapping, a piece of alloy metal in the shape of a bear was heated to roughly 30 °C, and was placed on a table; the printed array of sensors was placed over the bear with the contacts facing upward so the resistance at each point could be measured individually and sequentially using the source meter. The experiment setup was under IR camera, and the resulting image is shown in Figure 8c. The resistance of each pixel of the array was recorded, and a calibration curve was used to convert the measured resistance to a temperature (Figure 8d). The results indicate that the sensor array is able to map the temperature of the 2D object. A similar experiment was conducted using the 12 wt% composite and the results are shown in Figure S9, Supporting Information. In all of our experiments, the surrounding temperature ranged from 22 °C to 24 °C; it is expected that excessively hot or cold surroundings may have an effect on the measurements. In significantly cooler or warmer environments, devices should be recalibrated to obtain accurate results.

To engineer stretchable devices, meandering or serpentine shapes were fabricated by DIW (Figure 9). The 6 wt% composite
Figure 10. a) Schematic diagram of DIW flower shape temperature sensor structure using 6 wt% composite ink. b) Resistance variation with temperature in a range of 20–70 °C. c) Real-time temperature measurement of the hand surface and wrist (adult female).

ink was chosen for this application instead of the 8 wt% ink as it exhibits similar properties but results in less clogging of the nozzle during printing. The conductive and responsive 6 wt% composite ink was deposited on top of the Kapton film (Figure 9a), achieving good adhesion between the two layers. Figure 9b shows temperature dependent $I$-$V$ performance of meandering temperature sensor using 6 wt% composite ink here from 20 °C to 70 °C. As the voltage was swept from $-5$ to $+5$ V, a linear and symmetric response was observed for both types of samples. This linear relationship indicates that DIW-printed meandering sample, pressed rGO pattern, and rGO-PHB composites (Figure 4) exhibited ohmic behavior at a given temperature. The results in Figure 9c demonstrated that the device was nearly unresponsive when exposed to bending of up to 3% strain; the meandering devices are much less vulnerable to bending deformation than the drop-cast film devices. Figure 9d shows the printed meandering temperature sensor can be stretched and twisted without delamination of the functional layer. The entire printing process of printing a thin-layer PDMS substrate and then printing conductive inks, and the stretching test can be observed in the Movies S1 and S2, Supporting Information. Figure 9e shows the images of the meandering temperature sensor at relaxed (0% strain) and stretched (10% strain) states; the measured TCR values are all around $0.005°C^{-1}$. This value is slightly lower than the drop-coated film 6 wt% device ($0.006°C^{-1}$) mainly because of the difference in geometry. The DIW-printed lines are around 10 µm in thickness, which is much less thicker than the drop-casted films (80 µm). We also tested the real-time performance of the device on human temperature monitoring, listed in Figure 9f. The meandering device was initially measuring the temperature of the room, and was then applied rapidly to the surface of the forehead, held for about 2 s, and then removed. It can be seen that the response of this device exhibits very little time delay upon contact with or removal from the heated object. This rapid response can be attributed to the small thickness of the sensor used in the measurement (including active layer and encapsulant, approximately 100 µm in total), which allows for rapid heat transfer.

With the help of DIW, different shapes of sensors can be easily and quickly manufactured, with potential for scale-up. We designed a temperature-sensing patch in the shape of a flower comprised of a meandering pattern fabricated between two thin layers of PDMS, as shown in Figure 10a. The flower printing process can be observed in Movie S3, Supporting Information. The measured TCR value is $0.0046°C^{-1}$ using 6 wt% conductive ink, in Figure 10b. Figure 10c shows that the device is capable of detecting small human temperature difference with stable output data during human movement. Here, the patch was mounted on the hand surface and wrist area, and temperatures were recorded.

5. Conclusions

In this study, rGO was introduced as a nanofiller (at concentrations from 3 wt% to 12 wt%) in PHB polymer to fabricate temperature-responsive materials with negative TCR using a solution processing method. The TCR values of pure rGO powder and PHB-rGO composites are higher than or comparable to those of metals like nickel, suggesting that PHB/rGO composites are capable of being utilized as temperature-sensing devices. Both the room temperature resistivity and the variation in resistance as a function of temperature depends strongly on the wt% loading of the nanofiller. In terms of heating, below the percolation threshold, the composites are generally insulating and show little change in resistance as a function of temperature. Near the percolation threshold (3 wt% in this work), composites exhibited intermediate resistivities which varied strongly as a function of temperature. Above the percolation threshold, samples were reasonably conductive and underwent smaller but stable and repeatable reductions in resistance upon heating. Devices were fabricated on both flexible and stretchable substrates utilizing both drop-casting of the functional ink and DIW. Sensors fabricated with a meandering shape devices on PDMS substrates were stretchable and relatively impervious to bending. The measured TCR values
of DIW-printed devices are slightly smaller than the casted film device due to the smaller thickness of the DIW-printed devices.

Our work offered a strategy to fabricate arrays of temperature-responsive devices from conductive composites using solution-based methods including drop-casting and direct ink writing. These devices are made using inexpensive materials on polymer substrates, and the devices themselves can be reused. Arrays of printed, functional inks can be used to map the temperature of various items, and could, in the future, even be printed on non-planar surfaces. Due to the hydrophobicity of the polymer matrix of the composites, the conductive materials are water-resistant; these arrays could be useful for monitoring temperature profiles in wet environments, including in the body or underwater.

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.

Keywords
conductory polymer composites, direct ink writing, flexible temperature sensors, mobility, polyhydroxybutyrate (PHB), reduced graphene oxide

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