ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

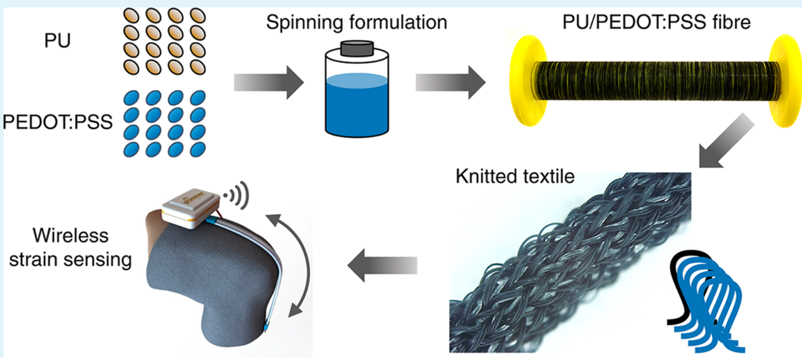
Knitted Strain Sensor Textiles of Highly Conductive All-Polymeric Fibers

Shayan Seyedin,[†,‡] Joselito M. Razal,[*,†,‡] Peter C. Innis,[†] Ali Jeiranikhameneh,[†] Stephen Beirne,[†] and Gordon G. Wallace[*,†]

[†]Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AIIM Facility, Innovation Campus, University of Wollongong, Wollongong, New South Wales 2522, Australia

[‡]Institute for Frontier Materials, Deakin University, Geelong, Victoria 3216, Australia

Supporting Information



ABSTRACT: A scaled-up fiber wet-spinning production of electrically conductive and highly stretchable PU/PEDOT:PSS fibers is demonstrated for the first time. The PU/PEDOT:PSS fibers possess the mechanical properties appropriate for knitting various textile structures. The knitted textiles exhibit strain sensing properties that were dependent upon the number of PU/PEDOT:PSS fibers used in knitting. The knitted textiles show sensitivity (as measured by the gauge factor) that increases with the number of PU/PEDOT:PSS fibers deployed. A highly stable sensor response was observed when four PU/PEDOT:PSS fibers were co-knitted with a commercial Spandex yarn. The knitted textile sensor can distinguish different magnitudes of applied strain with cyclically repeatable sensor responses at applied strains of up to 160%. When used in conjunction with a commercial wireless transmitter, the knitted textile responded well to the magnitude of bending deformations, demonstrating potential for remote strain sensing applications. The feasibility of an all-polymeric knitted textile wearable strain sensor was demonstrated in a knee sleeve prototype with application in personal training and rehabilitation following injury.

KEYWORDS: *strain sensors, composite fibers, knitted textiles, wet-spinning, polyurethane, PEDOT:PSS*

INTRODUCTION

Electronic components have been integrated within textile structures for a number of years to impart smart functionalities such as sensing, monitoring, energy storage, and information processing to traditional clothing.[1−8] Textiles offer suitable platforms with which to interact as they conform to the shape of human body and thus provide facile access to the functionality of the electronic equipment embedded within.[4,5,8,9] One application that benefits from this advantage is strain sensing. Strain sensors (or strain gauges) are devices that convert physical deformation into electrical signals. Traditional strain gauges are typically made of metals or rigid materials that offer limited stretchability and sensing range (typically less than 5% strain) making them unsuitable for practical applications if embedded within a textile structure.[10] Recently, a surge of interest has been directed toward the fabrication of flexible strain sensor devices.[11−14] Of particular importance are textile-based strain sensors that exploit the functionality of traditional textiles such as flexibility and wearability, and at the same time are capable of sensing strains larger than 5%.[15−18] Strain sensor textiles have important applications in body movement measurement,[15,18−20] medical monitoring,[21−23] sports rehabilitation and injury prevention,[24−26] and automobile safety belt.[27]

Several key factors must be considered in designing strain sensor textiles. The sensing response of the textile must be easily measurable (low resistance), and the measured electrical properties should correlate well to the magnitude of applied strain. The sensor should have high sensitivity (significant changes in the sensing response at different stretching conditions), high stability (repeatability of the sensing signals over many cycles) and large sensing range to cover the applied strain of the desired applications. To ensure a low time

Received: June 3, 2015
Accepted: September 3, 2015
Published: September 3, 2015

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

constant in the sensor response, the sensor structure should have high elastic properties and be able to recover rapidly from the deformation.[28] Finally, the sensor should be easily manufactured in large scale.[29]

A common mechanism of strain sensing is via resistive changes in the sensor device by strain offering ease of fabrication, simplicity of the sensing, large sensing range, high stability, and high sensitivity compared to other types of strain sensors such as capacitive.[30] In the resistive strain sensor textile (such as the one used here), the fabric serves as a resistor when a voltage is applied and changes its electrical properties with respect to the magnitude of the applied strain.[28]

The strain sensing property of a textile is closely related to its fabrication, structure, and to the sensing behavior of its components.[31] Textile strain sensors can be produced at the fiber, yarn, or fabric levels.[4,30] One method of fabricating strain sensor textiles is by coating a fabric with conducting materials such as polypyrrole,[25,32,33] poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS),[34] and carbon nanotubes.[35,36] However, mechanical mismatch with the textile typically results in crack formation, and subsequent electrical properties of the coated textile degrade under large deformations.[33] Textile strain sensor devices can also be made by knitting or weaving conducting fibers or yarns. Knitted steel yarns,[28] silver-coated nylon yarns,[30,37] and hand-knitted fibers of nitrile butadiene rubber filled with silver nanoparticles and multiwalled carbon nanotubes[17] are some examples of textile strain sensors in this category. It is highly desirable for the textile sensor to be made using conductive fibers or yarns, as this will enable the fabrication of sensors with the preferred structure and properties.[29] Furthermore, conductive fibers/yarns when knitted into the textile structures should be able to undergo large deformation before fracture to prevent fiber or yarn damage during the mechanical knitting process.[28] However, knitting using metallic fibers/yarns as the conductive component in the textile can result in structural damages as a result of high friction.[30] Further developments in this area requires fibers that are made of polymer or organic materials.[10] Polymer fibers offer less friction at the contact and the structure is maintained over a longer period of operation thereby increasing the life of the textile sensor. Furthermore, polymer fiber components can result in more flexible structures and improved wearability of the knitted textiles.

There are few literature reports on the production of strain sensor fibers from polymer or organic materials.[38−41] Those previously reported offer limited scalability and strain sensing properties (sensitivity, sensing range, and stability). We recently reported the fabrication of highly conductive polyurethane (PU)/PEDOT:PSS composite fibers that were capable of sensing over a large range of strains (up to ∼260%) when used as individual fibers.[41] In this work, we demonstrated that production of PU/PEDOT:PSS fibers could be scaled to produce continuously fiber lengths greater than 1000 m. More importantly, we demonstrated that these fibers possessed appropriate mechanical properties required for knitting either individually or together with yarns of similar mechanical properties. These knitted textiles provide an all-polymeric platform for large range strain sensing (up to 160% strain). To the best of our knowledge, this is the first report on the fabrication of strain sensor textiles from noncoated conducting elastomeric fibers.

By investigating a range of knitted textiles, we were able to develop a knitted textile strain sensor that exhibited low resistance, high sensitivity, high stability, and a large sensing range. A working prototype of a knitted textile sensor integrated with a wireless transmitter is demonstrated. This is the first time that all-polymeric composite fibers with strain sensing properties have been processed into textile structures using any form of textile machinery. This work highlights the promising potential of an all-polymeric conducting knitted fiber structure in a wearable intelligent textile application.

■ EXPERIMENTAL SECTION

Fiber Spinning. PU/PEDOT:PSS fiber spinning process has been described elsewhere.[41] Briefly, PU (AdvanSource Biomaterials Chronoflex C 80A) was dissolved in dimethyl sulfoxide (DMSO, Ajax Finechem) to achieve the polymer concentration of 10 mg mL^{-1}. PEDOT:PSS (1.5 mg mL^{-1}) pellets (Agfa Orgacon Dry, Batch No. A060000BY) were separately dispersed in DMSO by homogenization (Labtek IKA T25) at 15000 rpm for 30 min and mixed with the PU solution to produce the desired PU/PEDOT:PSS formulation (PEDOT:PSS 13.0 wt %). Fiber spinning was carried out using a wet-spinning method reported previously by our laboratory.[40−47] The scaled-up wet-spinning coagulation bath consisted of a vertical tubing (∼80 cm) on top of a horizontal bath (∼80 cm). Isopropanol/water mixture (80/20 v/v) was used as the nonsolvent into which the PU/PEDOT:PSS spinning formulation was injected using a 23 gauge needle (nozzle diameter ∼0.34 mm) spinneret at the controlled flow rate of 5 mL h^{-1}. We allowed the as-spun PU/PEDOT:PSS fibers to travel through an air gap of ∼70 cm for the nonsolvent evaporation and then continuously collected the fiber on a rotating winder with the aid of a linear guide. PU/PEDOT:PSS fibers were then transferred onto a spool for knitting (Figure S1).

Knitting. Knitting of the PU/PEDOT:PSS fibers were carried out using Harry Lucas (R1-S) circular knitting machine (head size, 1/12 in.; gauge, 28; 8 needles). The PU/PEDOT:PSS fibers were knitted into different structures as single-, double-, and four-ply individually and with a commercial Spandex (40 denier) or polyester (100 denier) yarn. The tension on the fibers was controlled to achieve uniform stich lengths throughout the structure.

Characterization. The PU/PEDOT:PSS fiber morphology was characterized using a field emission scanning electron microscope (JEOL JSM-7500FA) after sputter coating with gold (∼10 nm, EDWARDS Auto 306). An optical microscope (Leica DM EP) was used to observe the structure of the knitted PU/PEDOT:PSS fibers. The electromechanical properties of the knitted textiles were evaluated by in situ monitoring the resistance using a digital multimeter (Agilent 34410A) during cyclic deformations applied by a tensile testing instrument (Shimadzu EZ-L, 10 N load cell and 10 N clamps). A 1 cm length of the knitted textile was used for electromechanical testing. This length was chosen to achieve consistency with our previous report on the electromechanical testing of the individual PU/PEDOT:PSS fibers. The textile was clamped on the tensile instrument, and the electrical connections were established using copper tapes on the top and bottom clamps. Two pieces of rubber were used on each side of the textile to electrically insulate the structure and to avoid short circuit. The copper tapes were then connected to the digital multimeter (Agilent 34410A) using alligator clips and the resistance signal was acquired on a personal computer using an A/D interface. Two electromechanical tests were carried out. In the first test (referred to as the stability test), the textile was stretched to 100% strain and then allowed to relax (zero strain). A 30 s relaxation time was introduced after each loading and unloading step, and the test was carried out for 500 cycles. The second test (referred to as the range test) involved stretching of the textile to different applied strain magnitudes. The applied strain was increased from 40 to 200% in 20% incremental steps. The textile was stretched to the desired strain and then relaxed to 20% strain at the end of each stretching cycle with 30 s relaxation time between each loading and unloading step. The test was

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

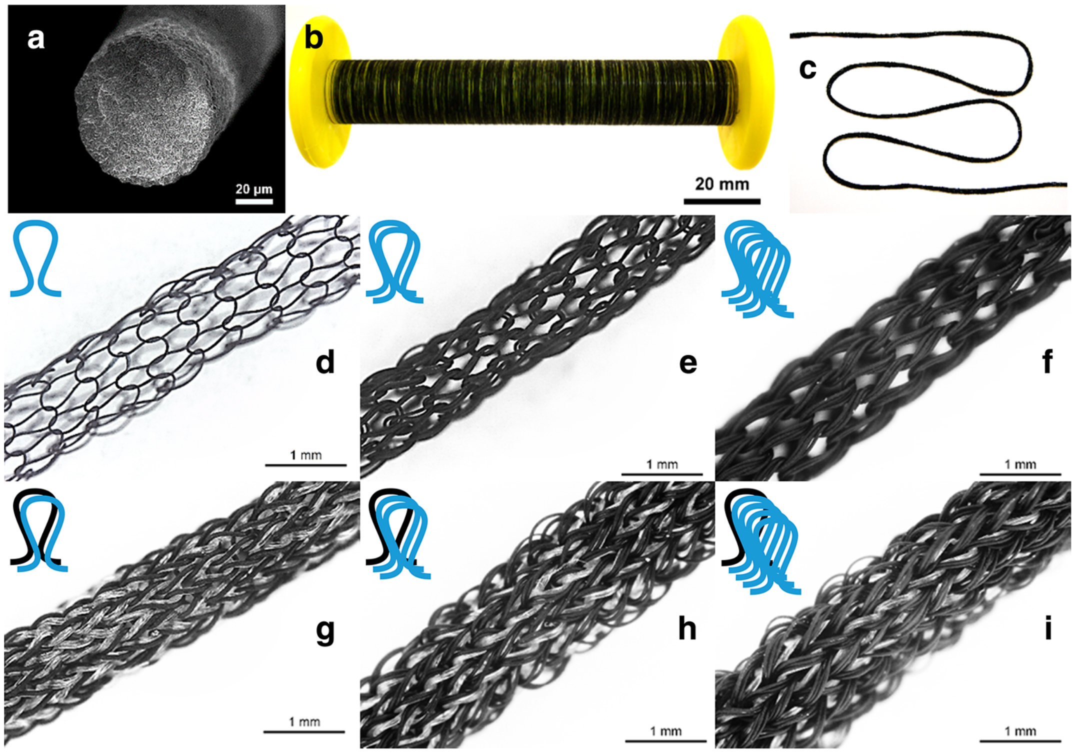


Figure 1. (a) SEM image of PU/PEDOT:PSS fiber with 13.0 wt % PEDOT:PSS; (b) PU/PEDOT:PSS fiber collected onto a spool after wet-spinning; (c) photograph of a typical PU/PEDOT:PSS fiber based knitted textile; optical microscopy images of the knitted (d) single, (e) double, and (f) four-ply PU/PEDOT:PSS fibers, and (g) single, (h) double, and (i) four-ply PU/PEDOT:PSS fibers co-knitted with a commercial Spandex yarn. The blue loop and the black loop represent PU/PEDOT:PSS fiber and Spandex yarn, respectively.

repeated for 50 cycles at each strain magnitude. Both of the electromechanical tests were carried out with the strain rate (crosshead speed) of 20 mm min^{-1} (200% min^{-1}).

Wireless strain sensing experiments were performed on a custom-built stretcher controlled by a LabVIEW interface and in-house 3D printed joints were used to apply extension by bending the textile. A 2.1 cm sample length of the knitted textile (compared to 1 cm used in electromechanical testing) was placed on the mechanical test rig and fixed with copper connectors. The test was carried out by cyclic bending the joints at different angles (30, 60, and 90°) at the rate of 180° min^{-1} (~250% min^{-1}) with 30 s relaxation time between each bending and straightening step. The knitted textile sensor was connected to a commercial Shimmer sensor via a voltage divider circuit and the signal was transmitted via Bluetooth to a personal computer and recorded.

A custom-coded program in Matlab computational software was used to analyze the results. The program measured the initial resistance (R_0, resistance at unstretched state), loading resistance ($R_{Loading}$), and unloading resistance ($R_{Unloading}$) by identifying the loading and unloading strains at each cycle and reporting the corresponding resistance values. The values of $\Delta R/R_0$ and gauge factors were then calculated from eqs 1 and 2, respectively (ε is applied strain in %).

$$\frac{\Delta R}{R_0} = \frac{R_{Loading} - R_{Unloading}}{R_0} \tag{1}$$

$$\text{gauge factor} = \frac{\Delta R}{\varepsilon R_0} \times 100 \tag{2}$$

■ RESULTS AND DISCUSSION

Scaled-up Fiber Production and Knitting. We took the advantage of the promising scalability of wet-spinning PU/PEDOT:PSS fibers in our previous report[41] and demonstrated here the production of continuous fibers with lengths exceeding 1000 m. The PU/PEDOT:PSS containing 13.0 wt % PEDOT:PSS loading with an electrical conductivity of ~9.4 S cm^{-1} and a Young's modulus of ~23.5 MPa, tensile strength of ~22.7 MPa, elongation at break of ~345%, and toughness of ~39.8 MJ m^{-3} was used in this work.[41] The isopropyl alcohol/water mixture (80/20 v/v) coagulation bath was used in the spinning process. Morphological observations under SEM confirmed that the PEDOT:PSS filler particles were dispersed very well within the PU parent elastomer and the cross-section of the fiber was circular and uniform along the fiber length (Figure 1a). Air-dried fibers that were transferred onto an appropriate spool for knitting is shown in Figure 1b.

The continuous fiber processing along with the outstanding mechanical properties of PU/PEDOT:PSS fibers has enabled the fabrication of knitted textile structures (Figure 1c–i). The PU/PEDOT:PSS fibers were knitted into plain stitch structures in the form of single-ply (Figure 1d), double-ply (Figure 1e), and four-ply (Figure 1f) using a circular weft knitting machine. The tubular structures consisted of 8 loops with diameters in the range of 1–2 mm. The same structures were also fabricated with the addition of a commercial Spandex yarn (Figure 1g–i). While the PU/PEDOT:PSS fibers can also be knitted with yarns of different linear densities and mechanical properties, such as polyester (Figure S1c), we have chosen the Spandex yarn for this application because it has mechanical properties similar to PU/PEDOT:PSS fibers.

Effect of Structure on Strain Sensing. The strain sensing properties of the knitted textiles were measured by in situ monitoring the resistance response during the cyclic tensile extension-relaxation tests in the wale direction (i.e., along the columns of loops) (Figure 2a). In the first set of experiments,

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150–21158

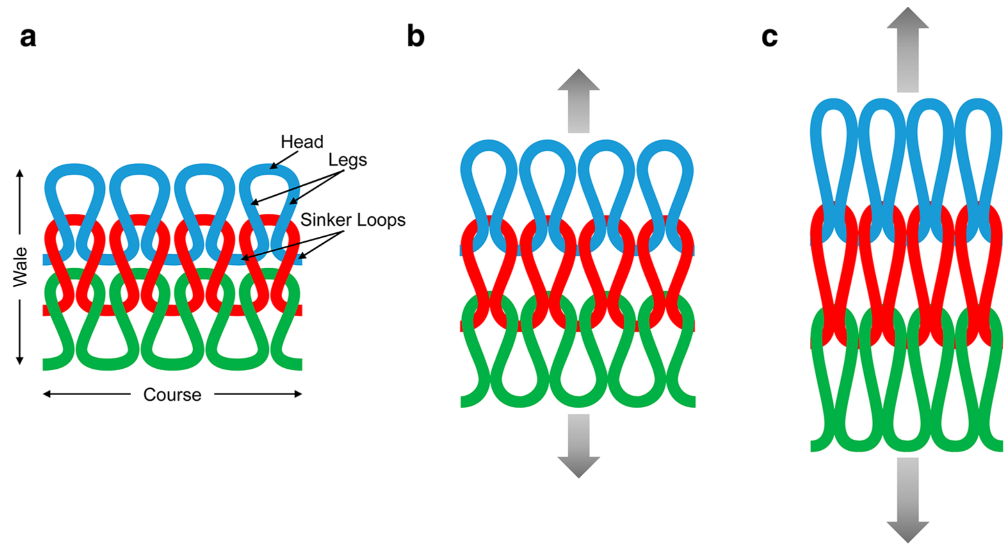


Figure 2. Schematic illustration of a weft-knitted textile with plain stitches at (a) unstretched and (b and c) different stretched states. Stretching is applied along the wale direction.

the stability of the knitted sensors' response was evaluated by cyclically stretching (and then relaxing) the textiles between zero and 100% strain. Figure 3a−d show the first 10, middle 10, and last 10 cycles of the stability tests (see Figure S2 for the graphs consisting of the whole data). For all textile structures, the resistance response decreased with stretching (loading) and increased upon relaxation (unloading). The resistance of the knitted textile sensors appeared to be highly stable after 500 cycles demonstrating reproducible strain sensing properties during the cyclic tests. The immediate change in resistance when the strain is applied or removed illustrates a fast response (within seconds) to tensile deformations (Figure S3). It was also found that the sensing response of the textiles changed with the structure of the knitted textile, that is, the number of PU/PEDOT:PSS fibers and Spandex yarn. The resistance decreased when the number of PU/PEDOT:PSS fibers within the textile was increased. Interestingly, the decrease in the resistance of the knitted textiles was proportional to the number of PU/PEDOT:PSS fibers used to make the textile. For example, the textile with four PU/PEODT:PSS fibers had 2 and 4 times lower resistance than the textile with two and one fiber, respectively (Figure 3a−c). The addition of a nonconductive Spandex yarn did not affect the conductivity of the textile (Figure 3d). It did, however, result in a significant enhancement of the stability of the sensor response. This can be seen in the constant level of resistance after unloading (the upper level of the resistance in Figure 3d). In contrast, the knitted textiles without the Spandex yarn (Figure 3a−c) exhibited an initial higher resistance levels (for ~10 cycles).

One of the performance metrics of a strain sensor is the gauge factor eq 2, which determines its sensitivity. Gauge factor is the relative change in the sensing response between the stretched and the unstretched states.[29,30] The gauge factors of the knitted sensor textiles were calculated from the electromechanical stability tests with applied strain between 0 and 100% (Figure 3e−h). It was observed that the knitted sensor textiles exhibited negative gauge factors (i.e., the resistance decreased with applied strain), in contrast to the positive gauge factor observed when PU/PEDOT:PSS fibers were tested as individual fibers (i.e., not knitted).[41] It is noted that negative gauge factor is desirable for many applications. For example, the decrease in resistance upon stretching can be used as a direct on/off switch for an LED or a buzzer indicator coupled to the strain sensor. Interestingly, it was observed that the absolute value of the gauge factor increased with the number (ply) of PU/PEDOT:PSS fibers in the knitted textile from ~ −0.2 for single-ply, to ~ −0.5 for double-ply, and ~ −1.0 for four-ply (Figure 3e−g). Also, the gauge factor did not change when a Spandex yarn was added to make a hybrid textile (Figure 3h). In all samples, the stability of the textile sensors improved after the first few cycles. It was also observed that the addition of a Spandex yarn resulted in a more stabilized linear behavior than the equivalent structure without the Spandex yarn throughout the whole 500 cycles (Figure 3g,h). The low resistance, negative gauge factor value, and high stability during the cyclic stretching of the hybrid textile present an outstanding platform for strain sensing application.

We correlated the electromechanical behavior of the knitted textile with the possible deformations that occur within a knitted structure. First, a knitted textile is made up of interlocks of rows (course) and columns (wale) of loops (Figure 2a). Each loop consists of a head, two legs, and two sinker loops that join the adjacent loops.[48] The difference in deformation properties along the course and wale directions results in an anisotropic property in the textile. The strain sensing properties of the knitted PU/PEDOT:PSS textiles was evaluated along the wale direction because the sensitivity and deformation range of a knitted sensor textile in this direction is much larger than the course direction.[31]

Furthermore, unlike in a woven structure where the resistance of the textile is independent of the fiber/yarn contact resistance, the contact resistance plays an important role in a knitted structure.[49] In knitted textiles, the conducting fiber in a loop makes contact with the adjacent loops at the heads, legs and sinker loops (Figure 2a).[28,30,31,49] The contact resistance (R_c) between the two fibers can be described by the Holm's theory[50] eq 3.

$$R_c = \frac{\rho}{2}\sqrt{\frac{\pi H}{nP}} \quad (3)$$

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

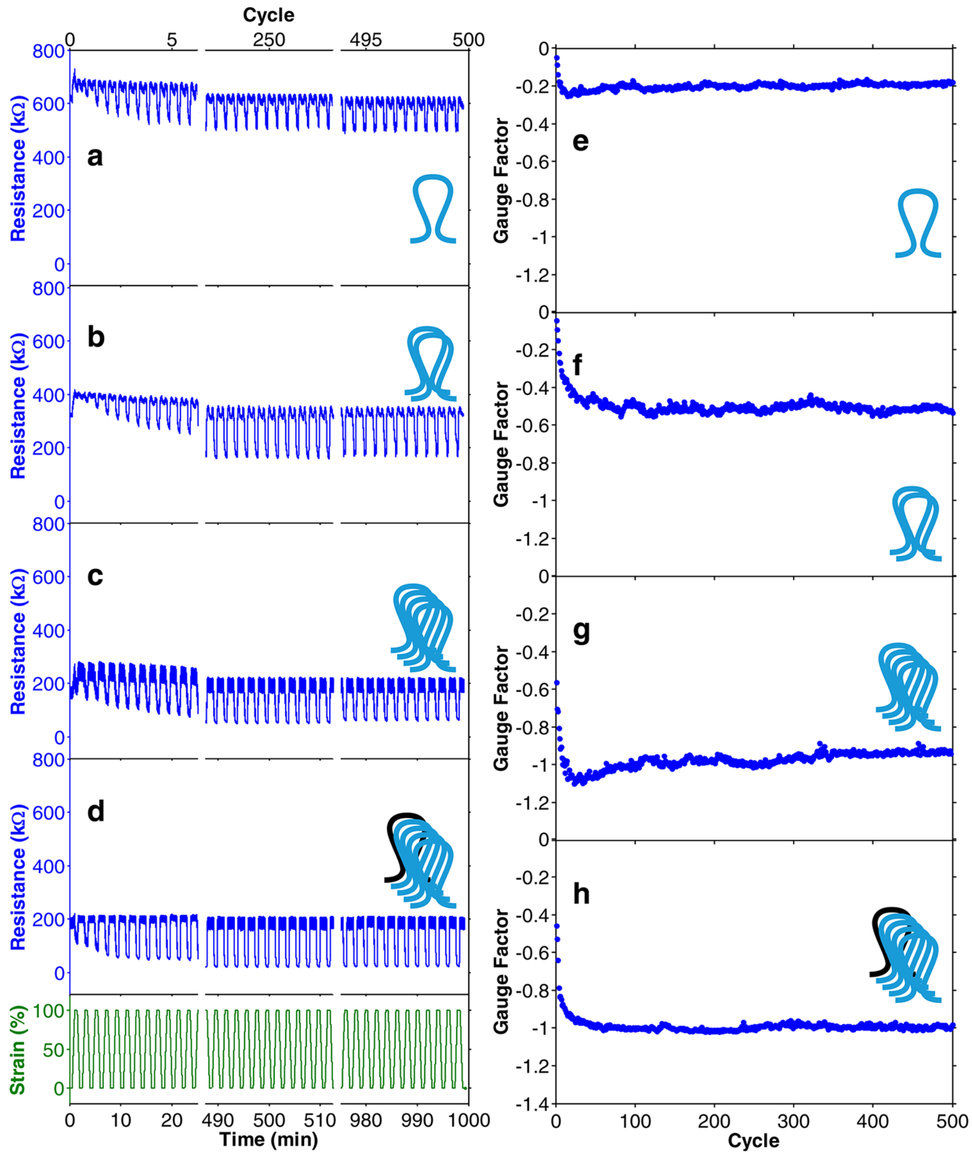


Figure 3. Electromechanical properties of the knitted textiles containing (a) single-ply, (b) double-ply, and (c) four-ply PU/PEDOT:PSS fiber. (d) Commercial Spandex yarn is co-knitted with four-ply PU/PEDOT:PSS fiber to make the hybrid textile. The data shown is for the first, middle, and last 10 cycles of the 500 cyclic test that was done between 0 and 100% strain. (e−h) Strain gauge plot for each sample shown as gauge factor vs. cycle.

where ρ is the resistivity of the fiber, n is the number of contact points (related to the number of PU/PEDOT:PSS fibers in the knitted textile), P is the contact pressure, and H is the fiber contact hardness. Stretching the textile in the wale direction results in an increased contact pressure between the interlocked fibers.[28,31,49] eq 3 shows that in a knitted textile, the contact resistance of the fibers at the interlocks will decrease with increasing the contact pressure and the number of contact points for a given fiber (assuming constant resistivity and hardness). Moreover, when a knitted textile is subjected to a uniaxial tensile strain in the wale direction, the configuration of the loops will change. The fiber segment in the head is bent, and the leg segments become longer (Figure 2b).[28,31,49] The increase in the length of the leg segments is due to the slippage and rearrangement of the fiber, which occurs when the tension applied on the fiber dominates the interfiber friction.[49] This deformation-induced lengthening of the legs results in an increase in the resistance in the leg segments of the textile.[28,31,49] The decrease in resistance of the knitted PU/PEDOT:PSS textiles upon stretching can be attributed to the lowering of interfiber contact resistance due to the enhanced contact pressure in the stretched state. This results in the negative gauge factor behavior of the knitted textiles.

It has been shown previously that the textile structures significantly affect the sensing properties such as the gauge factors, the sensing range, the linearity and the stability (repeatability).[30] Here, it is shown that by increasing the number of PU/PEDOT:PSS fibers in the knitted structure, a knitted textile with lower resistance, higher stability and linearity, and higher sensitivity (gauge factor value) is achieved. The lower resistance of the sensor textile knitted from four-ply PU/PEDOT:PSS fibers is due to the increased contact points and higher pressure on the interlocked fibers at the contact points as suggested by the Holm's contact resistance theory.[50]

Previous reports show that the sensitivity of a polymer-based strain sensor decreases when the electrical conductivity is

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

enhanced by the conductive filler.[51] Moreover, it has also been reported that compact knitted structures have low sensitivity (i.e., low gauge factor value).[37] In this work, increasing the number of the PU/PEDOT:PSS fibers during knitting (higher compactness) resulted in synergistic enhancements in electrical conductivity and gauge factor of the textile sensor. Furthermore, knitted structures with high elastic recovery have been shown to exhibit high stability.[28] This work also shows that the stability of the knitted textile can be improved by increasing the number of fibers during knitting as this method effectively improves the overall elasticity of the textile.

Effect of Applied Strain on Strain Sensing. The strain sensing behavior of the textile structure comprising of four-ply PU/PEDOT:PSS fibers and a Spandex yarn was further evaluated at applied strains of up to 180%. The electromechanical behavior of the knitted textile for this test is presented in Figure S4. From the measured minimum resistance ($R_{Loading}$) and maximum resistance ($R_{Unloading}$) data at each cycle, we calculated the $\Delta R/R_0$, and gauge factors. It can be seen that up to 160% strain, the unloading resistance increased with applied strain while the loading resistance remained relatively constant (Figure 4a). The distinct differences in $\Delta R/R_0$ for each applied strain in Figure 4b clearly show that the knitted textile sensor can distinguish the different magnitudes of applied strain. Notably, a highly stable sensor response was observed for each applied strain whereby the $\Delta R/R_0$ remained constant within the 50 cycles of testing. More importantly, the knitted textile sensor exhibited a constant (linear) gauge factor value of ∼ −1 at applied strains of up to 160% (Figure 4c). The sensor response deviated from linear behavior above 160% strain and this became more pronounced at 180%, which coincided with the onset of a significant increase in $R_{Loading}$ (Figure 4a).

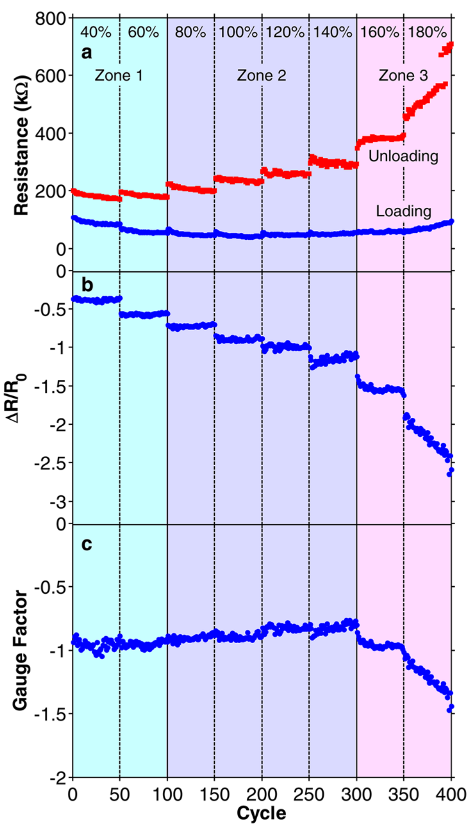


Figure 4. Strain sensing properties of knitted four-ply PU/PEDOT:PSS fibers and commercial Spandex yarn between 20 and 180% strain for 50 cycles: (a) loading and unloading resistance responses at each cycle, (b) $\Delta R/R_0$, and (c) gauge factor.

At high applied strains, the electromechanical behavior of the knitted textile is also influenced by changes in conductivity of the individual fibers that make up the textile. This is because the fiber becomes stretched only after the knitted textile is fully stretched (Figure 2c).[31] It also means that when the applied strain is not high enough to stretch the fiber, the configurational changes in the knitted structure will be the dominant factor in determining the electrical properties of the textile under strain.[28] However, when the applied strain is high enough to also stretch the fibers, the measured resistance of the textile reflect both the fibers' and the structural and configuration changes in the knitted textile.[30]

The electromechanical behavior of the knitted textiles tested under different levels of applied strain can be categorized into three distinct zones (Figure 4): 0−80% (zone 1), 80−160% (zone 2), and >160% (zone 3). In zone 1, the decrease in $R_{Loading}$ upon stretching is attributed mainly to the configurational changes in the textile structure. (i.e., the increased contact pressure between the conducting PU/PEDOT:PSS fibers). The $R_{Loading}$ remained constant in zone 2 which suggests that the interlocked structure attained between 80 and 160% strain result only in minimal stretching of the individual fiber.[31] Above 160% strain (zone 3), individual fibers are also stretched and contribute to strain sensing. Stretching of the individual fibers in this zone results in an increase of $R_{Loading}$. This effect is more pronounced in the $R_{Unloading}$, which suggests that the conductive network in the individual fiber is affected by further stretching, in accordance with our previous report.[41] The breakage of the conducting filler network within the individual PU/PEDOT:PSS fibers is responsible for the sudden increase in resistance after cyclic stretching at 180% (shown by the arrow on Figure S4). The optical images of the knitted textiles under different stretching conditions (Figure S5) reveal no evidence of damage or any kind of crack formation on the fibers during or after stretching. At the unstretched state, gaps were observed between the fibers and loops. Some of these gaps remained even after stretching the textile at 100% strain, suggesting that the individual fibers were not yet stretched. However, at 160% no gaps could be observed between the fibers in the textiles and the fibers were relatively parallel to the stretching direction suggesting that individual fibers were also stretched. When the applied strain is below 160%, the textile extension is only through the elongation of loops and legs, as well as bending of the heads. The rearrangement of the fibers result in enhanced contact between the fibers, thus lowering the resistance according to eq 3. Therefore, the strain sensing at applied strains <160% primarily comes from the configurational changes in the knitted structure because the change in resistance of the individual fiber is negligible. These results validate our claim that the fibers are only stretched at applied strains above 160% explaining the negative gauge factor behavior of the knitted textiles. The return of the fibers in the knitted textiles to their original configurations upon relaxation is also evident in this figure. It should be noted that surface friction prevents the complete recovery of the fibers to their original configuration in the textile structure. This results in the reduction of the contact pressure at the interlocks, which causes the $R_{Unloading}$ to differ at various applied strain

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

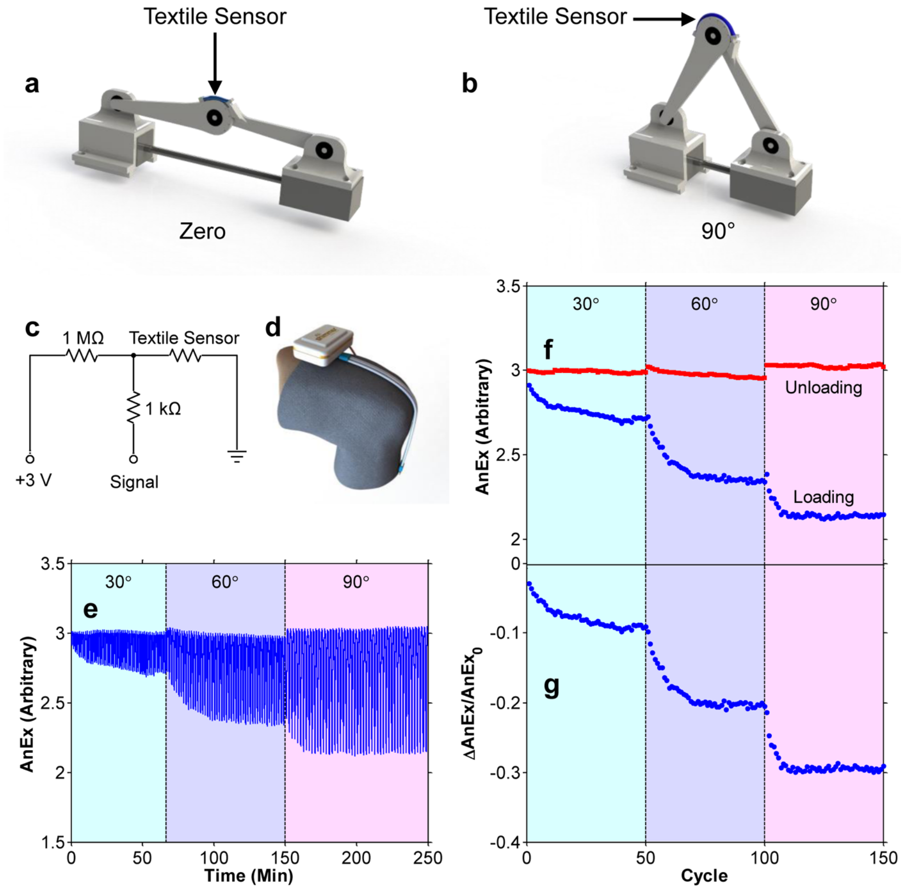


Figure 5. Wireless sensing of the knitted strain sensor textile. Schematic illustrations of the setup used for wireless strain sensing at initial (a, zero bending) and bent (b, 90° bending) states; (c) voltage divider circuit used to connect the textile sensor to the AnEx board of the Shimmer wireless sensor; (d) prototype knee sleeve; (e) wireless strain sensing behavior of the knitted sensor textile made from four-ply PU/PEDOT:SS fibers and commercial Spandex yarn; (f) loading and unloading wireless response of the sensor; and (g) relative changes of the wireless response at each cycle for the same test.

magnitudes.[28] The constant gauge factor in the zones 1 and 2 (up to 160% strain) demonstrates the linearity of the sensor's response suggesting that the relative change of resistance depends on the applied strain. This allows for the sensor's response to be easily correlated to the magnitude of applied strain.

The results presented here suggest that the knitted textile sensor can be used for applications that require strain sensing up to 160%. This sensing range is significantly higher than the previous reports on coated textiles (10−80%)[25,32−36] and knitted silver plated yarns (40%).[30,37] The very large range of strain sensing in this work can cater for a wide range of practical applications. For example, strain sensing up to ∼55% has been reported for the detection of limb movements.[15] The method we present also has the advantage over other approaches that it allows fabrication of strain sensor textiles with various structures, that is, different numbers of conducting elastomeric fibers and conventional fibers/yarns in various patterns. This ability is of crucial importance for integrating strain sensor fibers in commercial fabrics (i.e., by knitting or weaving).

Our textile strain sensor caters for the detection of relatively large magnitude of change in strain and has limitation toward detecting small strain changes (<5%). At high applied strains, however, it displays high stability and repeatability during cyclic stretching. The stable gauge factor at different strain magnitudes shown (up to 160%) suggests that the knitted textile sensor can measure a wide range of body movements reliably. We note that the relatively low gauge factors (∼ −1) of our textile strain sensors are due to the combination of large sensing range and low conductivity. Other reports which achieved large sensing range (up to 200%) also reported low gauge factors (∼0.06).[15] This suggests that in order to develop textile strain sensors with high gauge factor that operate at the equivalent large sensing range as ours, the textile component must possess high electrical conductivity. This is difficult to achieve with composite fibers without sacrificing their mechanical properties (particularly their stretchability). The strategy that we found more practical in increasing the gauge factor of the knitted textiles is by using multiple PU/PEDOT:PSS fibers in knitting the textile. It is also important to note that literature-reported strain sensors with high gauge factors have much lower sensing range (<80%) than our textile sensors.[25,32−37]

Wireless Strain Sensing. The PU/PEDOT:PSS fiber based knitted textile was integrated with a wireless transmitter to determine if the system was capable of sensing tensile and bending deformations with standard electronic interfaces. The knitted sensor textile structure (four-ply PU/PEDOT:PSS fibers with a Spandex yarn) was coupled with a commercially available Shimmer wireless sensor and used to measure bending deformations remotely. We used a custom-built system as shown in Figure 5a,b to apply bending extensions to the textile.

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158

The shimmer sensor response was monitored upon bending the textile between 0 and 90° at 30° increments. This setup was designed to mimic knee bending movements. Figure 5a,b show the system for the wireless strain sensing test at both initial (0° bending) and bent (90° bending) states of the joints. The wireless strain sensing experiments were carried out by connecting the knitted textile to the analog expansion (AnEx)[52] board of the Shimmer sensor using a simple voltage divider circuit consisting of two resistors (1 MΩ and 1 kΩ, Figure 5c). The AnEx board allows the Shimmer platform to connect to a third party analog devices such as the textile strain sensor in this case. It can be seen from the wireless response (AnEx) of the Shimmer that the textile sensor responded to the different levels of bending deformation (Figure 5e,f) similar to the observed changes in resistance when wired electromechanical tests were performed. In each case, the AnEx signal decreased when bent and then increased upon relaxation. Notably, the magnitude of the relative difference between the AnEx signals at bent and relaxed states increased with bending angle (Figure 5g). In each case, the AnEx response stabilized after several initial cycles. We observed consistent results from 2.1 cm knitted textile samples for the wireless strain sensing experiments with the 1 cm samples used in electromechanical testing. On the basis of the demonstrated wireless sensing capabilities of the knitted textile sensor, we built a prototype knee sleeve (Figure 5d) that could be strapped onto a knee and sense the bending movements (see Supporting Information for a video demonstration of the prototype). This knee sleeve has applications in sports injury prevention and rehabilitation as it can provide signals to the user during training or exercise.[25,26]

CONCLUSION

The continuous fabrication of highly conductive and highly stretchable PU/PEDOT:PSS composite fibers has enabled the knitting of various textile structures. The knitted textiles exhibited strain sensing properties which were notably structural dependent. By increasing the number of PU/PEDOT:PSS fibers in the textile, the resistance of the sensor decreased and the sensitivity (gauge factor) improved. Co-knitting the PU/PEDOT:PSS fibers with a commercial Spandex yarn yielded a textile sensor with a significantly higher stability. The textile sensor comprising of four-ply PU/PEDOT:PSS fibers co-knitted with a single Spandex yarn exhibited a highly stable response over a wide range of applied strain (up to 160%). More importantly, the relative resistance change was correlated with the strain magnitude resulting in a constant gauge factor. Furthermore, the knitted textile performed well when paired with a commercially available wireless sensor transmitter, which demonstrated the viability of the wireless strain sensing in a knee sleeve prototype. The facile manufacturing of all polymeric and wearable textiles presented here, combined with the large sensing range, high sensitivity, and high cyclic stability, make these knitted textile sensors attractive for practical applications such as remote body movement measurement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04892.

Images of fabricated conducting elastomeric fibers and the strain sensor textiles and measurements of their electromechanical properties. (PDF)

Demonstration of the prototype knee sleeve. (AVI)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: joselito.razal@deakin.edu.au.

*E-mail: gwallace@uow.edu.au.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from Australian Research Council (G.G.W. and P.C.I. on CE140100012, G.G.W. on FL110100196, and J.M.R. on FT130100380), the provision of facilities at the Australian National Fabrication Facility (Materials Node) and at the University of Wollongong Electron Microscopy Center, and the technical assistance of Dr. Javad Foroughi on knitting experiments.

REFERENCES

(1) Service, R. F. Technology. Electronic Textiles Charge Ahead. *Science* **2003**, *301*, 909−911.

(2) Park, S.; Jayaraman, S. Smart Textiles: Wearable Electronic Systems. *MRS Bull.* **2003**, *28*, 585−591.

(3) De Rossi, D. Electronic Textiles: A Logical Step. *Nat. Mater.* **2007**, *6*, 328−329.

(4) Coyle, S.; Wu, Y.; Lau, K.; De Rossi, D.; Wallace, G.; Diamond, D. Smart Nanotextiles: A Review of Materials and Applications. *MRS Bull.* **2007**, *32*, 434−442.

(5) Cherenack, K.; van Pieterson, L. Smart Textiles: Challenges and Opportunities. *J. Appl. Phys.* **2012**, *112*, 091301.

(6) Jost, K.; Dion, G.; Gogotsi, Y. Textile Energy Storage in Perspective. *J. Mater. Chem. A* **2014**, *2*, 10776−10787.

(7) Castano, L. M.; Flatau, A. B. Smart Fabric Sensors and E-Textile Technologies: A Review. *Smart Mater. Struct.* **2014**, *23*, 053001.

(8) Stoppa, M.; Chiolerio, A. Wearable Electronics and Smart Textiles: A Critical Review. *Sensors* **2014**, *14*, 11957−11992.

(9) Post, E. R.; Orth, M.; Russo, P. R.; Gershenfeld, N. E-Broidery: Design and Fabrication of Textile-Based Computing. *IBM Syst. J.* **2000**, *39*, 840−860.

(10) Cochrane, C.; Koncar, V.; Lewandowski, M.; Dufour, C. Design and Development of a Flexible Strain Sensor for Textile Structures Based on a Conductive Polymer Composite. *Sensors* **2007**, *7*, 473−492.

(11) Lipomi, D. J.; Vosgueritchian, M.; Tee, B. C.-K.; Hellstrom, S. L.; Lee, J. a; Fox, C. H.; Bao, Z. Skin-like Pressure and Strain Sensors Based on Transparent Elastic Films of Carbon Nanotubes. *Nat. Nanotechnol.* **2011**, *6*, 788−792.

(12) Park, M.; Im, J.; Shin, M.; Min, Y.; Park, J.; Cho, H.; Park, S.; Shim, M.-B.; Jeon, S.; Chung, D.-Y.; Bae, J.; Park, J.; Jeong, U.; Kim, K. Highly Stretchable Electric Circuits from a Composite Material of Silver Nanoparticles and Elastomeric Fibres. *Nat. Nanotechnol.* **2012**, *7*, 803−809.

(13) Robert, C.; Feller, J. F.; Castro, M. Sensing Skin for Strain Monitoring Made of PC-CNT Conductive Polymer Nanocomposite Sprayed Layer by Layer. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3508−3516.

(14) Chiolerio, A.; Roppolo, I.; Sangermano, M. Radical Diffusion Engineering: Tailored Nanocomposite Materials for Piezoresistive Inkjet Printed Strain Measurement. *RSC Adv.* **2013**, *3*, 3446−3452.

(15) Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.; Futaba, D. N.; Hata, K. A Stretchable Carbon

Nanotube Strain Sensor for Human-Motion Detection. *Nat. Nanotechnol.* **2011**, *6*, 296−301.
(16) Yan, C.; Wang, J.; Kang, W.; Cui, M.; Wang, X.; Foo, C. Y.; Chee, K. J.; Lee, P. S. Highly Stretchable Piezoresistive Graphene-Nanocellulose Nanopaper for Strain Sensors. *Adv. Mater.* **2014**, *26*, 2022−2027.
(17) Ma, R.; Lee, J.; Choi, D.; Moon, H.; Baik, S. Knitted Fabrics Made from Highly Conductive Stretchable Fibers. *Nano Lett.* **2014**, *14*, 1944−1951.
(18) Wang, Y.; Wang, L.; Yang, T.; Li, X.; Zang, X.; Zhu, M.; Wang, K.; Wu, D.; Zhu, H. Wearable and Highly Sensitive Graphene Strain Sensors for Human Motion Monitoring. *Adv. Funct. Mater.* **2014**, *24*, 4666−4670.
(19) Lorussi, F.; Scilingo, E. P.; Tesconi, M.; Tognetti, A.; De Rossi, D. Strain Sensing Fabric for Hand Posture and Gesture Monitoring. *IEEE Trans. Inf. Technol. Biomed.* **2005**, *9*, 372−381.
(20) Mattmann, C.; Clemens, F.; Tröster, G. Sensor for Measuring Strain in Textile. *Sensors* **2008**, *8*, 3719−3732.
(21) Carpi, F.; DeRossi, D. Electroactive Polymer-Based Devices for e-Textiles in Biomedicine. *IEEE Trans. Inf. Technol. Biomed.* **2005**, *9*, 295−318.
(22) Lymberis, A.; Olsson, S. Intelligent Biomedical Clothing for Personal Health and Disease Management: State of the Art and Future Vision. *Telemed. J. e-Health* **2003**, *9*, 379−386.
(23) Kubo, H. D.; Hill, B. C. Respiration Gated Radiotherapy Treatment: A Technical Study. *Phys. Med. Biol.* **1996**, *41*, 83−91.
(24) Gibbs, P. T.; Asada, H. H. Wearable Conductive Fiber Sensors for Multi-Axis Human Joint Angle Measurements. *J. Neuroeng. Rehabil.* **2005**, *2*, 7.
(25) Wu, J.; Zhou, D.; Too, C. O.; Wallace, G. G. Conducting Polymer Coated Lycra. *Synth. Met.* **2005**, *155*, 698−701.
(26) Munro, B. J.; Campbell, T. E.; Wallace, G. G.; Steele, J. R. The Intelligent Knee Sleeve: A Wearable Biofeedback Device. *Sens. Actuators, B* **2008**, *131*, 541−547.
(27) Hamdani, S.; Fernando, A. The Application of a Piezo-Resistive Cardiorespiratory Sensor System in an Automobile Safety Belt. *Sensors* **2015**, *15*, 7742−7753.
(28) Zhang, H.; Tao, X.; Yu, T.; Wang, S. Conductive Knitted Fabric as Large-Strain Gauge under High Temperature. *Sens. Actuators, A* **2006**, *126*, 129−140.
(29) Boland, C. S. C.; Khan, U.; Backes, C.; O'Neill, A.; McCauley, J.; Duane, S.; Shanker, R.; Liu, Y.; Jurewicz, I.; Dalton, A. B.; Coleman, J. N. Sensitive, High-Strain, High-Rate, Bodily Motion Sensors Based on Graphene-Rubber Composites. *ACS Nano* **2014**, *8*, 8819−8830.
(30) Atalay, O.; Kennon, W. R. Knitted Strain Sensors: Impact of Design Parameters on Sensing Properties. *Sensors* **2014**, *14*, 4712−4730.
(31) Wang, J.; Xue, P.; Tao, X.; Yu, T. Strain Sensing Behavior and Its Mechanisms of Electrically Conductive PPy-Coated Fabric. *Adv. Eng. Mater.* **2014**, *16*, 565−570.
(32) Li, Y.; Cheng, X. Y.; Leung, M. Y.; Tsang, J.; Tao, X. M.; Yuen, M. C. W. A Flexible Strain Sensor from Polypyrrole-Coated Fabrics. *Synth. Met.* **2005**, *155*, 89−94.
(33) Wang, J. P.; Xue, P.; Tao, X. M. Strain Sensing Behavior of Electrically Conductive Fibers Under Large Deformation. *Mater. Sci. Eng., A* **2011**, *528*, 2863−2869.
(34) Ding, Y.; Invernale, M. A.; Sotzing, G. A. Conductivity Trends of PEDOT-PSS Impregnated Fabric and the Effect of Conductivity on Electrochromic Textile. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1588−1593.
(35) in het Panhuis, M.; Wu, J.; Ashraf, S. a.; Wallace, G. G. Conducting Textiles from Single-Walled Carbon Nanotubes. *Synth. Met.* **2007**, *157*, 358−362.
(36) Zhang, R.; Deng, H.; Valenca, R.; Jin, J.; Fu, Q.; Bilotti, E.; Peijs, T. Carbon Nanotube Polymer Coatings for Textile Yarns with Good Strain Sensing Capability. *Sens. Actuators, A* **2012**, *179*, 83−91.
(37) Atalay, O.; Kennon, W. R.; Husain, M. D. Textile-Based Weft Knitted Strain Sensors: Effect of Fabric Parameters on Sensor Properties. *Sensors* **2013**, *13*, 11114−11127.
(38) Bilotti, E.; Zhang, R.; Deng, H.; Baxendale, M.; Peijs, T. Fabrication and Property Prediction of Conductive and Strain Sensing TPU/CNT Nanocomposite Fibres. *J. Mater. Chem.* **2010**, *20*, 9449−9455.
(39) Granero, A. J.; Razal, J. M.; Wallace, G. G.; in het Panhuis, M. Elastic conducting carbon nanotube-laden SIBS fibers. In *Proceedings of the 2010 International Conference on Nanoscience and Nanotechnology (ICONN)*, IEEE, Feb 22−26, 2010; Sydney, Australia: pp 80−83.
(40) Granero, A. J.; Wagner, P.; Wagner, K.; Razal, J. M.; Wallace, G. G.; in het Panhuis, M. Highly Stretchable Conducting SIBS-P3HT Fibers. *Adv. Funct. Mater.* **2011**, *21*, 955−962.
(41) Seyedin, M. Z.; Razal, J. M.; Innis, P. C.; Wallace, G. G. Strain-Responsive Polyurethane/PEDOT:PSS Elastomeric Composite Fibers with High Electrical Conductivity. *Adv. Funct. Mater.* **2014**, *24*, 2957−2966.
(42) Jalili, R.; Aboutalebi, S. H.; Esrafilzadeh, D.; Shepherd, R. L.; Chen, J.; Aminorroaya-Yamini, S.; Konstantinov, K.; Minett, A. I.; Razal, J. M.; Wallace, G. G. Scalable One-Step Wet-Spinning of Graphene Fibers and Yarns from Liquid Crystalline Dispersions of Graphene Oxide: Towards Multifunctional Textiles. *Adv. Funct. Mater.* **2013**, *23*, 5345−5354.
(43) Aboutalebi, S. H.; Jalili, R.; Esrafilzadeh, D.; Salari, M.; Gholamvand, Z.; Aminorroaya Yamini, S.; Konstantinov, K.; Shepherd, R. L.; Chen, J.; Moulton, S. E.; Innis, P. C.; Minett, A. I.; Razal, J. M.; Wallace, G. G. High-Performance Multifunctional Graphene Yarns: Toward Wearable All-Carbon Energy Storage Textiles. *ACS Nano* **2014**, *8*, 2456−2466.
(44) Jalili, R.; Razal, J. M.; Innis, P. C.; Wallace, G. G. One-Step Wet-Spinning Process of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Fibers and the Origin of Higher Electrical Conductivity. *Adv. Funct. Mater.* **2011**, *21*, 3363−3370.
(45) Jalili, R.; Razal, J. M.; Wallace, G. G. Exploiting High Quality PEDOT:PSS−SWNT Composite Formulations for Wet-Spinning Multifunctional Fibers. *J. Mater. Chem.* **2012**, *22*, 25174.
(46) Jalili, R.; Razal, J. M.; Wallace, G. G. Wet-spinning of PEDOT:PSS/Functionalized-SWNTs Composite: A Facile Route Toward Production of Strong and Highly Conducting Multifunctional Fibers. *Sci. Rep.* **2013**, *3*, 3438.
(47) Seyedin, M. Z.; Razal, J. M.; Innis, P. C.; Jalili, R.; Wallace, G. G. Achieving Outstanding Mechanical Performance in Reinforced Elastomeric Composite Fibers Using Large Sheets of Graphene Oxide. *Adv. Funct. Mater.* **2015**, *25*, 94−104.
(48) Spencer, D. J. *Knitting Technology: A Comprehensive Handbook and Practical Guide*, 3rd ed; Woodhead Publishing: Cambridge, U.K., 2001.
(49) Zhang, H. Electro-Mechanical Properties of Knitted Fabric Made From Conductive Multi-Filament Yarn Under Unidirectional Extension. *Text. Res. J.* **2005**, *75*, 598−606.
(50) Holm, R. *Electric Contacts: Theory and Applications*; 4th ed; Springer: New York, 1967.
(51) Hu, N.; Karube, Y.; Arai, M.; Watanabe, T.; Yan, C.; Li, Y.; Liu, Y.; Fukunaga, H. Investigation on Sensitivity of a Polymer/Carbon Nanotube Composite Strain Sensor. *Carbon* **2010**, *48*, 680−687.
(52) Burns, A.; Greene, B. R.; McGrath, M. J.; O'Shea, T. J.; Kuris, B.; Ayer, S. M.; Stroiescu, F.; Cionca, V. SHIMMER - A Wireless Sensor Platform for Noninvasive Biomedical Research. *IEEE Sens. J.* **2010**, *10*, 1527−1534.

DOI: 10.1021/acsami.5b04892
ACS Appl. Mater. Interfaces 2015, 7, 21150−21158