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Production and characterization of Graphene Nanoplatelet-based ink for smart textile strain sensors via screen printing technique

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- This study presents the development of a novel, biocompatible piezoresistive textile sensor.
- A water-based ink properly loaded with graphene nanoplatelets is deposited on a polyester fabric by a screen printing technique.
- The mechanical response of the screenprinted fabric is improved if compared to the one of the neat fabric.
- A high sensitivity (gauge factor) of about 30 for strains up to 5% was measured, even after water washing of coated fabrics.
- The proposed technique is promising and opens new routes to wearable strain sensor technology.

article info abstract

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Wearable systems are becoming highly attractive in different application areas. Recently, particular attention has been focused on the development of personal portable devices for monitoring occupational safety and health. Smart clothes based on strain sensors integrated on fabric seem to be a promising solution for real-time measurement of physiological endpoints. However, the development through a simple and cost-effective process of smart textiles characterized by high sensitivity, wearability and stable response even during physical activity, in case of exposition to environmental conditions and after washing is still challenging. In this work, the authors have developed a novel strain sensor made of graphene nanoplatelets (GNPs) properly dispersed into a water-based transparent ink, then deposited via screen printing technique on a synthetic fabric. Rheological investigations of the GNP-filled inks, morphological characterization of coated fabrics, electrical measurements of films obtained with different GNPs concentrations were performed. Smart textile specimens loaded with 3%wt and 3.8%wt of GNP-based inks were characterized through quasi-static tensile tests to investigate the electromechanical response, even after a washing cycle. Specimens have shown a sensitivity of about 30 for a strain of 5%. This performance is interesting for different applications such as monitoring of respiratory and heart rates. © 2020 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license ([http://](http://creativecommons.org/licenses/by-nc-nd/4.0/)

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1. Introduction

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The technological progress in the sector of electromechanical systems, of flexible electronics, the Internet of Things (IoT) and Industry

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Fig. 1. (a) Scheme of the fabrication process; (b) Picture of the screen printing setup; (c) Optical image of the screen printing frame.

4.0 has been the main driving force for the rapid growth of wearable technologies [\[1,2\]](#page-8-0). Nowadays, wearable sensors are used for monitoring biometric parameters in the medical and fitness fields, to increase the human physical and sensory capabilities and also to help to overcome some disabilities [3–[5\]](#page-8-0). Safety at work is a further area in which the use of wearable sensors and intelligent fabrics may play a key role for precautionary purposes. In fact, through these systems is possible to manage several risk situations (e.g., accidental falls, incorrect posture, wrong manual handling of loads) and to monitor worker stress as well as fatigue levels [6–[10](#page-8-0)].

Fig. 2. (a), (b) Equipment for electromechanical tests (c) Sketch of a screened fabric specimen with electrical contacts.

Although the sector of accessories and devices dominates the wearable landscape, smart fabrics are gaining more and more attention in the market and in academic research. In general, for a smart cloth it is required that all components are comfortable to wear, easy to use and washable as standard, reliable fabrics. However, traditional sensors are mostly bulky and can produce skin irritation. Therefore, to increase wearability and comfort, it is necessary to embed small, lightweight and pliable sensors as well as flexible electronic circuits into fabric, guaranteeing simultaneously their performance and functionalities. The sensor integration is a crucial process and of high technological interest. Possible solutions have been achieved through the development of new artificial fibers, yarns, embroidery, polymers, paints or inks which play the role of sensors thanks to their modified electrical properties [[11](#page-8-0)–14]. Such multifunctional materials have been integrated in the production of clothing in order to monitor different quantities of interest like biometric parameters [[15\]](#page-8-0).

Optical fibers (e.g., Fiber Bragg-Grating (FBG) sensors) has aroused particular interest in the development of smart textiles, since they enable simultaneous detection and transmission of signals. However, their application is limited due to their high costs, poor wearability and because makes the washing process extremely critical.

Other solutions have led to the use of conductive fibers to interconnect and integrate strain sensors in the fabric or of polymer sensors embedded which are applied directly on the textile [[16,17](#page-8-0)].

Fig. 3. Effective electrical conductivity of coatings obtained with the ink loaded with different GNP weight fractions.

The wide spreading of nanotechnologies and the consequent fabrication of new type of sensors exploitable in the wearable field are affecting the development of high-performance multifunctional smart textiles [\[18](#page-8-0)]. In fact, in the last few years, piezoresistive sensors including carbon nanotube (CNTs) or graphene have been extensively studied. Specifically, it was assessed that, due to its intrinsic properties, graphene is an extremely attractive candidate for printed and wearable electronics.

Stampfer et al. showed that a single CNT changes its resistivity as a function of the applied force [[19\]](#page-8-0). Cullinan and Culpepper, have experimentally validated a theoretical framework that clarifies the dependence of the intrinsic piezoresistivity of CNTs on their chiral angle and diameter. So, these characteristics drove the development of piezoresistive sensors based on CNTs [\[20\]](#page-8-0).

H. Souri et al. in [[18](#page-8-0)] produced electrically conductive yarns made of natural fibers coated with graphene nanoplatelets (GNPs) and carbon black (CB). The produced yarns were used to fabricate wearable, stretchable, and durable strain sensors with a gauge factor (GF) in the range of 1.46 to 5.62, depending on the magnitude of the applied strain and displacement rate. Flexible, stable and highly sensitive strain sensors were also fabricated by Tao Yan et al. in [\[21\]](#page-8-0) through the use of carbon/graphene composites nanofiber yarns (CNY) and thermoplastic polyurethane (TPU).

Currently, the focus has shifted to another type of sensors made of conductive inks directly printed on the fabric and able to absorb mechanical stresses elastically, while also maintaining appropriate levels of conductivity. Compared to conductive fibers, the printing of conductive varnish/inks on fabric shows many advantages in terms of flexibility and cost-effectiveness. Moreover, a technological novelty is related to the possibility to limit the deterioration of the circuits' electrical properties caused by repeated mechanical stress or washing cycles.

Significant results have been obtained through the functionalization of polymer-based paints and inks suitable for nanoparticles, to produce sensor prototypes easily applicable to fabrics by means of different printing techniques. However, the current limitations of this approach are related to the difficulties in the control of the dispersion and uniform distribution of fillers in the ink, the reproducibility of the sensor properties, reliability of the process and cytotoxicity of both process and nanostructures. Nevertheless, the production route of nanofilled inks seems to be promising and worth to be more deeply investigated and optimized for the specific application in smart fabrics. In fact, it can enable tailoring and designing properly the textile multifunctional properties, thus ensuring the possibility to obtain a better sensing capability compared to the one that can be achieved through a conventional sensor integration in clothes. As an example, Gualandi et al. have produced a chemical sensor, consisting of an organic electrochemical transistor made of a conductive polymer (PEDOT: PSS), which was fully integrated in a textile through screen printing processes [\[18](#page-8-0)]. In [[22\]](#page-8-0) P. Cataldi et al. have developed flexible and conductive (~10 Ω /sq) cotton fabrics through the impregnation with graphene-based thermoplastic polyurethane. The nanocomposite fabrics show a remarkable resistance to compression and tensile deformations as well as to washing cycles. Moreover, bend induced micro-cracks can easily be cured by hot pressing, also restoring the initial electrical conductivity. The nanocomposites maintain their breathability and resistance to environmental ageing when also exposed to solar radiation and high humidity. Young-Ju Kim et al. have produced in [[23](#page-8-0)] a graphene-based piezoresistive nanocomposite, which acts as a deformation sensor. The graphene/epoxy resin composites printed on a fabric show a symmetrical and reversible behavior and a GF of about 11.4.

The present work is the result of a research project related to the development of new sensorized textiles for monitoring the deformation of the rib cage following respiratory movement. Specifically, the elastic fabric is sensorized by screen printing a water-based ink suitably loaded with GNPs, thus creating piezoresistive sensors integrated into the fabric. In this paper, at first GNP-filled inks have been produced and

Fig. 4. Viscosity measurement as a function of the shear rate.

characterized from the rheological point of view in order to improve the nanomaterial dispersion process. Then, the electromechanical properties of the produced smart textiles have been assessed experimentally before and after consecutive washing cycles. The results demonstrate high sensitivity and stability of the developed smart fabric, showing a gage factor of 30 corresponding to an elongation of 5%.

2. Materials and methods

2.1. Production and deposition of conductive GNP-based ink

The fabrication process is sketched in [Fig. 1](#page-1-0)(a). GNPs were initially produced through the thermal expansion of graphite intercalated compound at 1150 °C for 5 s in a muffle furnace, the subsequent dispersion in acetone and tip sonication using an ultrasonic processor as described in [\[24\]](#page-8-0). The resulting GNP-acetone suspension was evaporated in oven at 90 °C for 30 min to ensure complete removal of the solvent. Next, the dried GNP powder was mixed with a water-based formaldehydefree commercial screen-printing paint (Transparent Texilac for Glitter LF) adding 5%wt of deionized water (DI) [[25](#page-8-0)]. After dispersing the GNP in the paint, mixing was carried out mechanically in order to prevent GNP agglomerations in the suspension.

Fig. 5. Shear Stress measurement as a function of the shear rate.

Fig. 6. SEM image of GNP based ink.

The deposition of the prepared inks was then performed on a weft knitting fabric composed of 96% of polyester and 4% of elastane yarns through a manual out-of-contact screen printing method. The system used is composed of an aluminum frame with a mesh of 55 weaved polyester threads ([Fig. 1](#page-1-0) (b), (c)). The angle of the mesh is 90° and

Fig. 7. SEM images of: surface (a) and cross-section (b) of the plain fabric; surface (c) of the fabric coated with the GNP-filled ink at 3%wt and surface (d) of the fabric coated with the GNP-filled ink at 3.8%wt; (e) SEM images of coated fibers; (f) SEM image of the coating on

the diameter of wires is approximately 80 μm. The distance between the mesh and the substrate (i.e., the fabric) is set equal to ~3 mm. All the samples were produced passing a rubber squeegee twice over the area of interest.

The screen-printed fabric with the GNP-filled ink was then placed in the oven at 150 °C for 3 min, to complete the polymerization.

Notice that different weight fractions of GNPs were considered, even if, as it will be explained in the next section, the GNP concentrations of 3%wt and 3.8%wt were finally selected for rheological and piezoresistive tests, with the scope of achieving the best compromise between screen printing workability of the resulting composite and a proper value of electrical conductivity, required for the specific strain sensing application [\[26\]](#page-8-0).

2.2. Rheological characterization

Rheological characterization was carried out using an Anton Paar MCR302 Rheometer, available in Sapienza Nanotechnology and Nanoscience Laboratory (SNN-Lab) at Sapienza University. The rotational rheometer was equipped with two flat parallel plates with a gap of 0.7 mm. The measurements were carried out at room temperature, with a shear rate ranging from 1 s⁻¹ to 1000 s⁻¹.

Scope of the rheological measurements was to compare the viscoelastic properties of the produced GNP-filled ink with the ones of the unloaded ink, in order to optimize the sensor production process corresponding to the specific concentration of fillers needed to achieve the targeted performances of the fabrics.

Fig. 8. Stress-Strain curve for knitted fabric in wales and courses direction.

Fig. 9. Mechanical behavior of the fabric coated with neat ink and GNP based ink at 3%wt and 3.8%wt of GNPs.

2.3. Morphological characterization

The morphology of the coated fabric samples was studied using a Zeiss Auriga Field Emission scanning electron microscopy (SEM) available at SNN-Lab. The samples' surface was coated with a 15 nm-thick Cr layer by using a Quorum Tech Q150T sputter. The imaging of materials was produced at different magnifications.

2.4. Electrical characterization

In order to perform electrical tests and to investigate the effect of the amount of GNPs on the effective electrical conductivity of filled paint, five films of inks loaded at 2, 2.5, 3, 3.5 and 4%wt of GNPs were produced on Mylar substrates via the tape casting deposition method. The average thicknesses of coatings were all around 50 μm. Five small samples, $(2 \text{ cm} \times 2 \text{ cm})$ in size, for each concentration were obtained by cutting the coated Mylar substrates with a blade and contacted through a conducting silver-based paint. Volt-amperometric measurements were then performed between the two opposite contacts of each specimen. The effective electrical conductivity was extracted from the values of the measured resistance, considering the size and thickness of produced specimens.

2.5. Mechanical and electromechanical characterizations

The stress-strain responses of the used synthetic fabric were obtained performing quasi-static tensile mechanical tests. Electromechanical tests were aimed at investigating the piezoresistive behavior of coated fabrics samples.

Neat and screened fabrics were cut into rectangular strips with dimensions of 150 mm x 25 mm. As shown in [Fig. 2\(](#page-1-0)c), coated fabric samples were also provided of electrical contacts. The electrical contacts were embroidered by silver fibers threads through a "back stitch" seam assuring a good continuity of the thread in the fabric and, hence a stable response during electrical measurements.

An Instron 3366 universal testing machine equipped with a 500 N load cell was used to perform the tensile tests on the produced samples. In particular, the top and bottom parts of the specimen were inserted in the screw side action tensile grips of the machine, as shown in [Fig. 2](#page-1-0)(a).

The piezoresistive response of the coated fabric samples was then evaluated through the resistance measurements as function of the applied tensile stress up to a maximum strain of 5% [[27](#page-8-0)]. In particular, the voltamperometric measurements, at room temperature (i.e., 23 \pm 3 °C) were performed using a Keithley 6221 dc/ac current source and a Keithley 2182a nano-voltmeter ([Fig. 2](#page-1-0)(b)).

The produced samples were subjected to three consecutive electromechanical tests. During each test the initial resistance R_0 (at rest condition) was recorded, after the tensile load release and the time necessary for its value stabilization.

Next to the first electromechanical cycle, the samples were washed. Firstly, fabric samples were put under running deionized (DI) water for 1 h. Then, they were left in a bath for 11 h and subsequently dried in air for 24 h. Finally, the samples were subjected to another electromechanical cycle of three consecutive tests.

Fig. 10. Resistance versus time during the electromechanical tests cycle of the sample containing GNPs at (a) 3.0%wt and (b) 3.8%wt before water-wash.

3. Result and discussion

3.1. Electrical and rheological characterization results

In [Fig. 3](#page-1-0) we reported the effective electrical conductivity of coatings on Mylar substrates obtained with inks loaded with GNPs at different weight fractions, ranging from 2%wt up to 4.5%wt. It results that the electrical conductivity of the deposited coatings increases with the GNP weight percentage; moreover it is also noted that for concentrations lower than 2.5%wt the electrical conductivity decreases rapidly.

The produced inks filled with the different GNP weight fractions (ranging from 2%wt to 4.5%wt) were deposited on the synthetic fabric via the screen printing method, as described in Section 2.1. For a filler amount higher than 4%wt we noticed that, even though the obtained ink was still well homogeneous and the viscosity manageable, after curing the ink deposited on textile was characterized by small cracks and defects. Moreover, same attempts to use concentrations of GNPs higher than 5%wt demonstrated the enormous difficulties in obtaining well dispersed nanoparticles within the polymeric matrix. Therefore, we decided to investigate more in details the rheological properties and electromechanical behavior (described in the following Section) of only two types of samples, the ones produced with GNPs at 3%wt (which guarantees the electrical response to be sufficiently away from the percolation threshold) and 3.8%wt. In particular we selected specifically the latter concentrations because, interpolating the results of [Fig. 3,](#page-1-0) it results that the obtained effective electrical conductivity $(10.26 \pm 1.5 \text{ S/m})$ is almost exactly twice the one of specimens at 3%wt of GNPs.

The rheological measurements were performed with the final aim to investigate the filled ink viscosity as function of the shear rate.

It is known that the major factors influencing the rheological response of GNP-polymeric composite are: matrix viscosity; nature of the nanoparticles; size distribution; interaction and maximum packaging fraction [\[28](#page-8-0)]. Moreover, there are additional factors that must be considered, like average diameter of the nanoparticles and degree of agglomeration, which affect both the mixing times and the final mechanical properties of the ink [29–[32\]](#page-8-0).

In order to obtain a composite material characterized by a good workability comparable to that of the unfilled ink, it was necessary to add solvent during the mixing phase. According to the ink datasheet, DI water can be used as solvent with a maximum weight concentration of 5% with respect to the matrix. Therefore, through the monitoring of the viscosity of the ink added with 5%wt of DI water and GNPs, we assessed the maximum amount of nanofiller that could be dispersed in the matrix in order to guarantee a rheological response of the filled ink similar to the one of the plain ink, at the shear rates simulating the screen printing process (around $1000 s⁻¹$).

[Fig. 4](#page-2-0) shows the measured viscosity as a function of the shear rate. The viscosity, due to the pseudoplastic behavior of the ink decreases with the shear rate [[29,33](#page-8-0)]; the ink is a non-Newtonian fluid showing a shear-thinning behavior. Moreover, the gap between the viscosity of the neat ink and of the loaded inks tends to reduce as the rotation speed of the rheometer plate increases due to ordering of GNPs induced by the flow [[34](#page-8-0)]. When the shear rate exceeds the value of about 100 s−¹ , we noticed that the viscosity of the loaded inks starts to decrease more rapidly. Therefore, due to the lubricant effect of GNPs the curve obtained for the loaded inks intersects the one corresponding to the neat ink at ~500 s⁻¹ [35–[37\]](#page-8-0).

The rheological behavior of the ink can be justified, at a microscopic level, as an ordering of the fluid molecules. For weak shear forces, the molecules are disordered and intertwined; when an increasing stress is applied, the polymer chains unravel in the direction of the applied stress. The alignment of the molecules or particles allows them to slide over each other and this leads to a decrease in viscosity [\[38](#page-8-0)]. The results are indicative of a good degree of mixing and dispersion of the filler in the matrix.

[Fig. 5](#page-2-0) shows the flow curves of the shear stress as a function of the shear rate. It is noted that for low shear rates the material has a shear stress value other than zero; this means that material flow occurs only when the applied stress exceeds τ_0 , which is the so called "sliding" limit" or "yield stress". This behavior is typical of Bingham pseudoplastic fluids, which are characterized by a minimum value of the shear stress, i.e. τ_0 , below which there is no sliding of the polymer chains ($\tau < \tau_0$) [28]. Nano-filled inks are characterized by a higher shear stress than neat ink. This can be justified by the fact that the ink/filler system requires more effort to orient both the polymer chains and the filler in the direction of the strain, allowing the chains to slide on top of each other [\[39\]](#page-8-0).

In conclusion, the analysis of results demonstrates that only at lower shear rates GNP-filled inks have higher values of both viscosity and shear stress than the neat ink and that samples loaded with 3%wt and

Fig. 11. Resistance versus time during the electromechanical tests cycle of the sample containing GNPs at (a) 3.0%wt and (b) 3.8%wt after water-wash.

Fig. 12. Measured resistance R0 of the sensors as a function of the number of electromechanical cycles, for the two GNP concentrations (i.e., 3%wt and 3.8%wt), before and after water-wash.

3.8%wt of GNPs shows similar rheological behavior. On the contrary, the results at higher shear rates indicate that the ink filled with GNPs at 3% wt has a better workability than the one with 3.8%wt of GNPs.

3.2. SEM images

SEM micrographs have been performed with the aim of investigating the integration between matrix and filler, and the degree of surface uniformity and homogeneity of the film. [Fig. 6](#page-3-0) shows images of GNPs on the ink surface after curing. The produced GNPs have an average thickness of 10 nm with a maximum value of about 20 nm and lateral dimensions around 1–2 μm [\[40,41\]](#page-8-0). It can be also noted a good integration between filler and polymer matrix.

Images of both the uncoated polyester fabric and of the two samples coated with inks filled with GNPs at 3%wt and 3.8%wt are reported. [Figs. 7](#page-3-0) (a) and (b) show respectively the surface and cross section of the neat fabric, in which the individual polyester fibers composing the yarns of the textile are clearly visible. It is possible to observe that the diameter of a single fiber and yarn is around 12 μm and 170 μm, respectively.

From the comparison of the micrographs in [Figs. 7](#page-3-0) (c) and (d), we notice that the surface of the textile coated with GNP-filled ink at 3% wt is characterized by a higher roughness than the surface of the samples with the ink filled with GNPs at 3.8%wt, which is smoother but with more defects. Such defects are micrometer-scale material inhomogeneities, like the voids depicted in [Fig. 7](#page-3-0) (d). We believe that they are attributable to the higher viscosity of the nanomaterial that cannot fully penetrate the interstices between the fabric yarns as it happens instead for the ink with GNP concentration of 3%wt.

The SEM images in [Fig. 7](#page-3-0) (f) show the GNP-filled ink deposited on the top of a fiber. After analyzing several images, we noticed that both films present an average thickness of 3 ± 1 µm. It is also worth to add that, due to the fabric roughness and interstices among fibers and among yarns, the screen-printed coating does not have in practice a constant thickness since the ink tends to partially fill the inter-yarn porosity.

3.3. Mechanical and electromechanical results

Since knitted fabrics are anisotropic materials the mechanical tests were firstly performed on samples cut both in the course and wale direction with the tensile force applied always in the same direction.

As shown in [Fig. 8,](#page-3-0) the stress of the knitted fabric has the highest value at a specific strain when the sample is cut in wale direction. This

Fig. 13. Sensitivity as function of the deformation: (a) Fabric printed with ink filled with GNPs at 3%wt and 3.8%wt, before and after washing; (b) Fabric printed with ink filled with GNPs at 3%wt, after the first deformation cycle, before and after washing; (c) Fabric printed with ink filled with GNPs at 3.8%wt after the first deformation cycle, before and after washing.

Table I

Sensitivity at specific strain values of strain sensors integrated into fabrics through screen printing technique using different loaded inks.

result, which is in agreement with what has been shown in other works [[42\]](#page-8-0) demonstrates that the resistance to extension of considered fabric is higher in the wale direction then in the course one.

Since the GNP/ink-based coating, due to its piezoresistive property, manifests an electrical resistance change as higher as more significant is the applied stretching, we decided to focus our attention on the mechanical and electromechanical behavior of wale-wise direction-cut coated fabric samples (representing the worst case-scenario). In [Fig. 9](#page-4-0), we show the comparison between the mechanical properties of fabrics coated with GNP-loaded inks and fabric coated with neat ink, in order to better highlight the effect of nanofillers on the mechanical response of the material. It is noted that the presence of GNPs increases inevitably the stiffness of the coated fabric.

Then, the piezoresistive responses of the sensors made of the screenprinted fabric using the ink loaded at 3%wt and at 3.8%wt of GNPs were assessed through measurements of the DC electrical resistance versus strain, as described in paragraph 2.4. The variations of the sensors' response after the washing cycle was also investigated.

[Figs. 10 and 11](#page-4-0) show the measured resistance as a function of time during the tensile elongation up to a maximum strain of 5% (occurred approximately after 100 s) and after the load release (up to 800 s). In particular, the curves refer to the results recorded in pre-wash [\(Fig. 10](#page-4-0) (a), (b)) and post-wash ([Fig. 11](#page-5-0) (a), (b)) conditions, respectively, obtained during the three consecutive tests (electromechanical cycle).

In accordance with what reported in section 3.1, the sample with 3.8%wt GNP showed a lower resistance values than that at 3%wt. It is also observed that the sensor resistance R_0 increased after the first test for both type of samples, before as well as after washing. This aspect is better highlighted in [Fig. 12](#page-6-0).

The increase in R_0 is assumed to be due to the stabilization of the material after the first mechanical stress test and it is originated by the fact that the inter-distances between adjacent GNPs in the polymeric ink changes when the sensor is subjected to an applied load. This implies a reorganization of the conducting network, which assumes a stable configuration after only one load cycle.

It is also shown that the resistance vs. time curves recorded during the second test are almost overlapping with those obtained during the subsequent test. That applies to both types of sensors, before and after washing, confirming the good repeatability of the electromechanical responses.

The sensitivity of the produced sensors was then evaluated using the gauge factor definition:

$$
GF = \frac{\Delta R}{\varepsilon R_0} \tag{1}
$$

in which ΔR, the variation of the sensor resistance due to the applied strain ε is normalized with respect to the initial value R_0 . The results are reported in [Fig. 13](#page-6-0).

In particular, [Fig. 13](#page-6-0) (a) shows the sensitivity of the sensors made with the ink loaded at 3%wt and 3.8%wt of GNPs, respectively, before and after washing, during the first electromechanical test. In [Figs. 13](#page-6-0) (b) and 13 (c) we reported the sensitivities of the sensors during the second and third electromechanical test, before and after washing. The results show a better consistency of GNP 3%wt sample in relation to the repeatability of the tests. This can be justified also considering the results of the rheological tests, which showed that samples with the lower content of GNPs were characterized by a better workability and consequently a better integration in the textile.

Finally, the performances of the produced smart textiles are compared in Table I with the ones of state-of-art strain sensors, as reported in recent literature to the best of our knowledge, obtained using other types of electrical conducting ink fillers (CNT, multi-walled carbon nanotubes (MWCNT), Ag nanowires (NWs)) and integrated into fabrics through screen printing techniques. Itis clearly highlighted that our solution allows to obtain the piezoresistive response with the highest sensitivity at a strain of 5% if compared with the others reported in the table.

4. Conclusions

In this work an innovative technique for the production of a piezoresistive fabric based on a water-based ink loaded with GNPs was proposed. The adopted out-of-contact screen printing process has demonstrated the feasibility of producing sensorized fabrics using a commercial ink properly loaded with graphene nanoplatelets.

Through the deposition technique it is possible to size the geometry of the sensor, whereas the electrical characteristics are optimized by the dispersion procedure of the nanometric filler inside the ink. The process is reproducible and easily scalable.

The sensors were fabricated and tested under controlled laboratory environmental conditions, that is a temperature of ~23 °C and relative humidity of ~40%.

The quasi-static mechanical tests on the screen-printed fabric, compared to the neat fabric, showed an increase of the stiffness of the material after the coating process, dependent on the filler weight fraction. The electromechanical tests, aimed at assessing the piezoresistive response of the coated fabrics, have shown an increasing sensitivity with strain: the results showed a GF of ~30 at maximum strain (5%) and a good repeatability throughout work cycles, in particular even after the washing process.

In conclusion, a piezoresistive material with highly sensitive and repeatable behavior was integrated on a synthetic fabric. Considering results and the range of deformation investigated, a possible exploitation could be in the field of wearable electronics focused to the monitoring of different biometric parameters such as respiration or heart rate.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of Competing Interest

None.

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Author Contribution Statements

Fabrizio Marra, Maria Sabrina Sarto, Alessio Tamburrano, Serena Minutillo conceived of the presented idea. Fabrizio Marra, Serena Minutillo carried out the experiments. Alessio Tamburrano, Fabrizio Marra, Serena Minutillo performed the Electrical and Electromechanical tests. Alessio Tamburrano verified the analytical methods. Maria Sabrina Sarto encouraged to investigate and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

References

- [1] [A. Bozkurt, Wearable Technology: the Current State of the Art, EDULEARN17 Proc, 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0005) [\(2017\) 8704](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0005)–8711.
- [2] [P. Bonato, Wearable sensors/systems and their impact on biomedical engineering,](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0010) [IEEE Eng. Med. Biol. Mag. 22 \(2003\) 18](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0010)–20.
- [3] [P.O.F. Well-being, Discussion paper monitoring technology : the 21St century](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0015) ' S, [EU-OSHA Discuss. Pap. \(2017\) 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0015)–10.
- [4] [I. Pavón, L. Sigcha, P. Arezes, N. Costa, G. Arcas, J.M. López, Wearable technology for](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0020) [occupational risk assessment: potential avenues for applications, Occup. Saf. Hyg. VI](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0020) [- Sel. Contrib. from Int. Symp. Occup. Saf. Hyg. SHO 2018 \(2018\) 447](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0020)–452.
- [5] [A. Lymberis, A. Dittmar, Advanced wearable health systems and applications re](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0025)[search and development efforts in the European union, IEEE Eng. Med. Biol. Mag.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0025) [26 \(2007\) 29](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0025)–33.
- [6] S. Wilson, R. Laing, Wearable Technology: Present and Future, 91st World Conf, Text, Inst, 2018. [https://www.researchgate.net/publication/327542210_Wearable_Tech](https://www.researchgate.net/publication/327542210_Wearable_Technology_Present_and_Future)[nology_Present_and_Future](https://www.researchgate.net/publication/327542210_Wearable_Technology_Present_and_Future).
- [7] S. Majumder, T. Mondal, M.J. Deen, Wearable sensors for remote health monitoring, Sensors (Switzerland). 17 (2017).
- [8] [S.D. Deshmukh, S.N. Shilaskar, Wearable sensors and patient monitoring system: a](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0035) [review, 2015 Int, Conf. Pervasive Comput. Adv. Commun. Technol. Appl. Soc. ICPC](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0035) [2015 \(00\) \(2015\) 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0035)–3.
- [9] [H. Cao, Smart Technology for Personal Protective Equipment and Clothing,](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0040) [Woodhead Publishing Limited, 2013](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0040).
- [10] [G.M.N. Islam, A. Ali, S. Collie, Textile sensors for wearable applications: a compre](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0045)[hensive review, Cellulose. 27 \(2020\) 6103](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0045)–6131.
- [11] L.M. Castano, A.B. Flatau, Smart fabric sensors and e-textile technologies: A review, Smart Mater. Struct. 23 (2014).
- [12] [M. Tomaney, Sustainable Textile Production, Elsevier Ltd 2015](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0050).
- [13] [F. Kane, Nonwovens in Smart Clothes and Wearable Technologies, Woodhead Pub](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0055)[lishing Limited, 2009](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0055).
- [14] [E. Shim, Smart Surface Treatments for Textiles for Protection, Woodhead Publishing](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0060) [Limited, 2013](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0060).
- [15] [A. Schwarz, L. Van Langenhove, P. Guermonprez, D. Deguillemont, A roadmap on](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0065) [smart textiles, Text. Prog. 42 \(2010\) 99](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0065)–180.
- [16] D. Lo Presti, C. Massaroni, J. D'[Abbraccio, L. Massari, M. Caponero, U.G. Longo, D.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0070) [Formica, C.M. Oddo, E. Schena, Wearable system based on](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0070) flexible fbg for respiratory [and cardiac monitoring, IEEE Sensors J. 19 \(2019\) 7391](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0070)–7398.
- [17] K. Cherenack, L. Van Pieterson, Smart textiles: Challenges and opportunities, I. Appl. Phys. 112 (2012).
- [18] I. Gualandi, M. Marzocchi, A. Achilli, D. Cavedale, A. Bonfiglio, B. Fraboni, Textile Organic Electrochemical Transistors as a Platform for Wearable Biosensors, Sci. Rep. 6 (2016)
- [19] C. Stampfer, A. Jungen, R. Linderman, D. Obergfell, S. Roth, C. Hierold. Nano[electromechanical displacement sensing based on single-walled carbon nanotubes,](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0075) [Nano Lett. 6 \(2006\) 1449](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0075)–1453.
- [20] [M.A. Cullinan, M.L. Culpepper, Carbon nanotubes as piezoresistive](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0080) [microelectromechanical sensors: theory and experiment, Phys. Rev. B - Condens.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0080) [Matter Mater. Phys. 82 \(2010\) 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0080)–6.
- [21] [T. Yan, Z. Wang, Y.Q. Wang, Z.J. Pan, Carbon/graphene composite nano](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0085)fiber yarns for [highly sensitive strain sensors, Mater. Des. 143 \(2018\) 214](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0085)–223.
- [22] [P. Cataldi, L. Ceseracciu, A. Athanassiou, I.S. Bayer, Healable cotton-Graphene Nano](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0090)[composite conductor for wearable electronics, ACS Appl. Mater. Interfaces 9 \(2017\)](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0090) 13825–[13830.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0090)
- [23] [Y.J. Kim, J.Y. Cha, H. Ham, H. Huh, D.S. So, I. Kang, Preparation of piezoresistive nano](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0095) [smart hybrid material based on graphene, in: Curr, Appl. Phys. 11 \(1\) \(2011\)](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0095) [350](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0095)–352.
- [24] M.S. Sarto, A.G. D'Aloia, A. Tamburrano, G. De Bellis, Synthesis, modeling, and experimental characterization of graphite nanoplatelet-based composites for EMC applications, IEEE Trans. Electromagn. Compat. 54 (2012).
- [25] Eptanova, Texilac Trasparente per Glitter LF, T.D.S. REV (2018). [https://www.](https://www.eptanova.com/sites/default/files/download_products/texilac-trasparente-per-glitter-lf-eng_0.pdf) eptanova.com/sites/default/fi[les/download_products/texilac-trasparente-per-glit](https://www.eptanova.com/sites/default/files/download_products/texilac-trasparente-per-glitter-lf-eng_0.pdf)[ter-lf-eng_0.pdf](https://www.eptanova.com/sites/default/files/download_products/texilac-trasparente-per-glitter-lf-eng_0.pdf).
- [26] E. Skrzetuska, M. Puchalski, I. Kruciń[ska, Chemically driven printed textile sensors](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0100) [based on graphene and carbon nanotubes, Sensors \(Switzerland\). 14 \(2014\)](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0100) 16816–[16828.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0100)
- [27] [C. Massaroni, J. Di Tocco, D. Lo Presti, U.G. Longo, S. Miccinilli, S. Sterzi, D. Formica, P.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0105) [Saccomandi, E. Schena, Smart textile based on piezoresistive sensing elements for](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0105) [respiratory monitoring, IEEE Sensors J. 19 \(2019\) 7718](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0105)–7725.
- [28] [M.M. Rueda, M.C. Auscher, R. Fulchiron, T. Périé, G. Martin, P. Sonntag, P. Cassagnau,](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0110) Rheology and applications of highly fi[lled polymers: a review of current under](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0110)[standing, Prog. Polym. Sci. 66 \(2017\) 22](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0110)–53.
- [29] [D.M. Kalyon, D. Dalwadi, M. Erol, E. Birinci, C. Tsenoglu, Rheological behavior of con](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0115)[centrated suspensions as affected by the dynamics of the mixing process, Rheol.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0115) [Acta 45 \(2006\) 641](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0115)–658.
- [30] D.-M. Liu, W.J. Tseng, Infl[uence of powder agglomerates on the structure and rheo](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0120)[logical behavior of injection-molded zirconia-wax suspensions, J. Am. Ceram. Soc.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0120) [82 \(2004\) 2647](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0120)–2652.
- [31] [C. Carrot, B. Olalla, R. Fulchiron, Relaxation of loose agglomerates of magnesium hy](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0125)[droxide in a polymer melt, Polymer \(Guildf\). 53 \(2012\) 5560](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0125)–5567.
- [32] D.M. Kalyon, S. Aktaş[, Factors affecting the rheology and Processability of highly](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0130) fi[lled suspensions, Annu. Rev. Chem. Biomol. Eng. 5 \(2014\) 229](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0130)–254.
- [33] [J.C. Chu, K.C. Burridge, F. Brown, The viscosity of pseudo-plastic](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0135) fluids, Chem. Eng. [Sci. 3 \(1954\) 229](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0135)–247.
- [34] [D.B. Genovese, Shear rheology of hard-sphere, dispersed, and aggregated suspen](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0140)sions, and fi[ller-matrix composites, Adv. Colloid Interf. Sci. 171](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0140)–172 (2012) 1–16.
- [35] [C.Y. Ho, S. Yusup, C.V. Soon, M.T. Arpin, Rheological behaviour of Graphene Nano](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0145)[sheets in hydrogenated oil-based drilling](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0145) fluid, Procedia Eng. 148 (2016) 49–56.
- [36] [K. Arapov, E. Rubingh, R. Abbel, J. Laven, G. De With, H. Friedrich, Conductive screen](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0150) [printing inks by gelation of Graphene dispersions, Adv. Funct. Mater. 26 \(2016\)](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0150) [586](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0150)–593.
- [37] [D.R. Saini, A.V. Shenoy, V.M. Nadkarni, Melt rheology of highly loaded ferrite-](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0155)filled [polymer composites, Polym. Compos. 7 \(1986\) 193](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0155)–200.
- [38] K. Luo, X. Wei, B. Huang, M. Yu, Influence of fi[ller on the rheological properties of uv](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0160) [curable offset ink, Appl. Mech. Mater. 200 \(2012\) 666](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0160)–669.
- [39] [T. Mezger, The Rheology Handbook: For Users of Rotational and Oscillatory Rheom](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0165)[eters, 2nd ed., 2002](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0165).
- [40] I. Bellagamba, F. Boccuni, R. Ferrante, F. Tombolini, F. Marra, M.S. Sarto, S. Iavicoli, Workers ' Exposure Assessment during the Production of Graphene Nanoplatelets in R & D Laboratory, (2020) 1–23.
- [41] M.S. Sarto, A.G. D'[Aloia, A. Tamburrano, G. De Bellis, Synthesis, modeling, and exper](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0170)[imental characterization of graphite nanoplatelet-based composites for EMC appli](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0170)[cations, IEEE Trans. Electromagn. Compat. 54 \(2012\) 17](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0170)–27.
- [42] Ž. Penava, D.Š. Penava, L. Miloš[, Experimental and analytical analyses of the knitted](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0175) [fabric off-axes tensile test, Text. Res. J. \(2020\) 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0175)–11.
- [43] [M.S. Sadi, M. Yang, L. Luo, D. Cheng, G. Cai, X. Wang, Direct screen printing of single](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0180)[faced conductive cotton fabrics for strain sensing, electrical heating and color chang](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0180)[ing, Cellulose. 26 \(2019\) 6179](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0180)–6188.
- [44] [C. Luo, B. Tian, Q. Liu, Y. Feng, W. Wu, One-step-printed, highly sensitive, textile](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0185)[based, tunable performance strain sensors for human motion detection, Adv.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0185) [Mater. Technol. 5 \(2020\) 1](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0185)–8.
- [45] I. Kruciń[ska, E. Skrzetuska, W. Urbaniak-Domagala, Prototypes of carbon nanotube](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0190)[based textile sensors manufactured by the screen printing method, Fibres Text. East.](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0190) [Eur. 91 \(2012\) 79](http://refhub.elsevier.com/S0264-1275(20)30842-X/rf0190)–83.