Flax fibers – epoxy with embedded nanocomposite sensors to design lightweight smart bio-composites

K. M. Tripathi, F. Vincent, M. Castro and J. F. Feller* (1)

Abstract Lightweight smart bio-composites with damage sensing ability have been designed. Conductive polymer nanocomposites-based quantum resistive sensors (sQRS) have been embedded in a unidirectional flax fibers – epoxy bio-composite samples using a spray layer by layer process to monitor their structural health and eventually anticipate their failure. The in situ piezo-resistive responses of sQRS under monotonic and incremental cyclic tensile tests were analyzed to learn more about the damage mechanisms and predict behavior changes in the laminated bio-composites. sQRS signals were found to be well correlated with the typical mechanical traces of flax fibers/epoxy composites, thus allowing reliable conclusions about structural changes taking place in the core of the bio-composite under strain. In particular, the analysis of sQRS gauge factor evolution with strain level proved to be helpful to assess the probability of damage. This new contribution to the understanding of flax fiber-based composites’ mechanical behavior is expected to be of special interest as the sliding of fibrils weakly assembled in bundles makes it difficult to approach.

Keywords Bio-composite, Conductive Polymer nanocomposites, Structural health monitoring, Quantum resistive, Strain sensors, Smart material

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Introduction

The development of lightweight composite materials for transports such as automotive, aerospace, and ships is of increasing interest since weight reduction is inversely proportional to energy consumption and can therefore enhance energy efficiency. Although traditional thermoset composites offer a high performance to weight ratio, their environmental footprint remains high due to the fact that they are neither bio-based nor easily recyclable. If the application does not require exceptional mechanical performances, several alternatives can be used to decrease the environmental impact of fiber-reinforced polymer composites (FRPC) by saving both energy and using non-renewable matter (by order of difficulty): (a) substituting thermosets chemically recyclable matrices like poly(ester) or poly(ether) UP by thermoplastic physically recyclable matrices such as poly(ether ketone) PEEK or poly(ether imide) PEI, (b) substituting petrol-based polymer matrices with recycled or bio-based polymer matrices such as poly(lactic acid) PLA of poly(amide 12) PA12, (c) substituting long carbon fibers by recycled short carbon fibers or substituting energy-consuming glass fibers (GF) by water-consuming renewable fibers such as flax (FF) or hemp (HF). Natural fibers can have comparable specific mechanical properties, i.e. modulus/density ratio, a lower environmental footprint, and are potentially biodegradable. A judicious combination of these strategies, would result in eco-composites with sufficient mechanical properties, such as flax fibers-reinforced poly(lactic acid) composites FF/PLA, for example. However, PLA is still considered as a too brittle matrix for automotive applications. Thus, in the meanwhile a new high-performance bio-based thermoplastic matrix is found, the more classical poly(ester) (EP) matrix has been preferred over PLA to facilitate the understanding of damage detection in FF-based composites. The complexity of the damage mechanisms of bio-composites results from their multiple origins: matrix crack, fiber/matrix interface debonding, fibril/fibril interface failure inside pectin and polysaccharide binder. Thus, in situ monitoring of the damage evolution in bio-composites before their catastrophic failure, could increase their reliability and eventually trigger maintenance operations.

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However, the existing sensing systems used for structural health monitoring (SHM) have several drawbacks that prevent their use in lightweight structures. Classical metallic gauges can only measure the strain on the surface of a material (the core is not inspected). Their sensitivity is modest with a gage factor (GF) close to 2, and their range is limited to the elastic limit preventing to monitor the plastic deformation and the damage accumulation in the composite. Their difference in dilatation with the composite substrate can yield important resistance drift and interfacial stress upon temperature variations that could compromise their sticking, which is often a critical point particularly during fatigue of impact solicitations.

Other systems for strain sensing such as fiber optic sensors (FOS), extrinsic Fabry-Perot interferometer (EFPI), and fiber Bragg grating (FBG) sensors can be integrated in the core of composites to follow precisely their deformation, but due to their larger dimension (about 10 times the diameter of reinforcing fibers without the protective coating), they can compromise the integrity of the composite. Moreover, the location of the areas of critical strain level causing the composite’s failure, is crucial to accurately set a limit state and determine the integration sites of the FOS by modeling. Therefore, the classical strain sensors used alone are not likely to follow the damage of composites and need to be combined with acoustic emission sensor (AE) to detect the damage in a material during a dynamic deformation process. But these sensors require to be organized in a complex network in the composite unlikely to be widely developed in large diffusion parts. Additionally, load conditions below the threshold of damage propagation remain theoretically unrecorded as AE emission monitoring registers only progressive defects, although high AE emissions have been recorded in healthy part without any explanation.

Compared to these different systems, piezo-resistive sensing, also promising for SHM of composite materials, has nevertheless different strategies to sense the deformation of the composites with conductive polymer nanocomposites (CPC):

(i) using CPC fibers highly or poorly filled with carbon nanotubes (CNT), or reinforcing fibers sized with a CPC coating or grafted with CNT that are embedded in the composites between plies, (fiber sensing),

(ii) using a CNT network percolated in the matrix, (bulk sensing),

(iii) using a CPC film deposited on the surface, (skin sensing),

(iv) using a CPC layer that can be located at the interphase between fibers and the matrix or between plies, (interphase sensing).

All these sensors can record the deformation and eventually damage of composite parts by monitoring resistance variations of a sensitive network of percolated conducting entities. However, integrating non-intrusive homogeneous sensors in the vicinity of the damage to understand the composite’s failure mechanism is still a challenge.

Additionally, there are some limitations associated to each strategy:

(i) Using a conducting network made of CNT without binder can lead to slippage between the nanotubes, only weakly bonded by van der Waals’ interactions at their junction points. This can also decrease strain transfer through the whole sensor, degrading strain measurements, and eventually weakening the composite. Therefore, as recently demonstrated by micro-debonding experiments, sensors are more robust when CNT are dispersed in a polymer matrix prior to their assembly in a percolated network.

(ii) Using a conducting network in close contact with fibers is likely to prevent the monitoring of carbon fiber-based composites that will be making shortcuts with CNT, but it may be possible to monitor damage by connecting directly carbon fibers as reported in early works.

(iii) Using bulk sensing allows to monitor globally a part, but makes it hard to achieve a homogeneous CNT network. Considering that CNT may be segregated during the composite’s processing, as it can be the case during vacuum infusion or even compression, the conducting network can hardly have a reproducible architecture. Moreover, the polymer’s viscosity is generally increasing exponentially with CNT content, which requires to adapt industrial formulations and devices.

(iv) Using fiber sensing requires to coat, or spin the fibers individually or already assembled in a strand of textile, prior to composites processing which is bringing additional steps in the fabrication.

In this context, the fabrication of sensing nanocomposite films via spray layer-by-layer (sLbL) that already proved to be very promising to make sensing skins for strain monitoring of textiles, and composites, presents many advantages such as:

(i) Dispersion: nanofillers are more effectively dispersed in solution by sonication than in more viscous liquid polymers under sheering,

(ii) Architecture: the ability to control the resistance of the sensing film step by step and the conducting architecture at different scales from nano to micro is of great interest,

(iii) Location: the possibility to localize the sensor in the core or on the surface of the composite and to adapt the size of the sensor to the need,

(iv) Versatility: the spray process is compatible with most composites’ processing techniques used in industry and do not require strong modifications of fabrication tools.

Concerning the implementation of strain sensing into bio-composites, the only attempt, to our knowledge, was made by Mader et al. They showed the sensitivity of a model composite sample, composed of a single fiber of jute coated with multiwall carbon nanotubes and embedded in a poly(epoxy) matrix, to moisture, temperature, and strain. It
is thus of interest to further study the strain sensing of unidirectional flax fibers-based smart composites. In such material, since all components are electrically insulating, the structuring of a CNT conductive network either directly in the polymer matrix, or on the fibers as a skin at the surface of the composite is possible. Among all, sLbL appears to be a versatile, reproducible, and reliable processing technique to tailor sensing properties and therefore allow the robust fabrication of implantable Quantum Resistive strain Sensors (sQRS). These sensors are also homogeneous and can follow the material behavior in a wider range of deformation than traditionally used metal foil; they can also be used for the characterization of the interface of natural fibers opening the way to bio-inspired smart, multiscale interfacial materials. But to localizing sensors in the vicinity of the damage and understand the composite failure mechanism remains a challenge.

In the present work, interfacial sQRS are integrated in a bio-composite to provide smart functionalities such as SHM. Conductive polymer nanocomposite sensors are fabricated in situ by sLbL at the flax fibers/epoxy matrix interface to follow both deformation and damage of bio-composite samples. The combined analysis of mechanical and electrical responses is used to better understand the failure mechanisms and transition between the elastic domain and the irrecoverable damage zone.

**Experimental**

**Materials**

Mats and unidirectional (UD) flax fibers (FF), of density \( \rho = 1.5 \, \text{g cm}^{-1} \) harvested in France were purchased from BIOINFORTIS® (France). Multiwall carbon nanotubes (NC-7000, CNT) with 90% purity and \( \rho = 1.4 \, \text{g cm}^{-1} \) density were kindly provided from NANOXYL® (Belgium). These CNT with average diameter \( D \approx 10 \, \text{nm} \) and length \( L \approx 1.5 \, \mu\text{m} \) were synthesized by CVD process. CNT were used as received without any further purification or surface modification. An EPOCIL 2020 epoxy resin (EP) AXSON (France) was used as matrix, and further mixed with its amine hardener in the 75:25 ratio. Chloroform was provided by ALDRICH (France) and used as received.

**Processing**

**Formulation of the nanocomposite solution**

Conductive polymer nanocomposite (CPC) formulations were synthesized simply by dispersing carbon nanotubes into an epoxy solution in chloroform in order to obtain a final concentration of 2 wt. % CNT in EP after homogenization (90 min at 25 °C under sonication with a BRANSON 3510) and further degassing (5 min). The final concentration of the CPC solution used for spraying was \([\text{CPC}] = 6.7 \, \text{g dm}^{-3}\). Chloroform was chosen due to its ability to dissolve poly(epoxy) and properly wet flax fibers’ surface.

**Fabrication of strain Quantum Resistive Sensors by spray Layer by Layer**

Strain Quantum Resistive Sensors (sQRS) were built in situ by spraying layer-by-layer (sLbL) conductive polymer nanocomposite (CPC) solutions directly on flax fibers’ surface with a homemade device allowing a precise control of nozzle scanning speed (10 cm s\(^{-1}\)), solution flow rate (50 mm sec\(^{-1}\)), stream pressure (0.20 MPa), and target to nozzle distance (8 cm) as also described in previous works.

The final thickness of sensors can be controlled by the number of layer sprayed. Generally, 10–50 layers are sprayed, depending on samples and applications. The sensors have a surface of about \( S < 0.5 \, \text{cm}^2 \) and a thickness in the range of \( 1.5 \, \mu\text{m} \). The sensors thickness was measured with an AFM after spraying sLbL the CPC solution directly onto a silicon wafer. The same conditions of fabrication as for sQRS integrated between FF plies (too rough for AFM observation) were used. Fig. 1 illustrates schematically the key steps of fabrication, including the sQRS localization and the structure of the poly(epoxy)/flax fiber bio-composite samples used for piezo-resistive characterization tests. Electrical connections were made with 0.05 mm yarns of carbon fibers with conductive silver paint as represented in Fig. 1. As the sensor is composed of the same polymer as that of flax laminates and considering its tiny thickness compared to fibers, it is expected that its presence will not influence the mechanical properties of the bio-composite, so that it can be considered as non-intrusive according to previous experiments on model microcomposites.

**Fabrication of bio-composites by vacuum bagging**

Epoxy/flax bio-composites (EP/FF) were fabricated using a hand lay-up procedure with a vacuum bagging technique at 600 mm Hg (800 hPa) pressure in order to reduce porosities and obtain composite of uniform thickness. Two sQRS were embedded in the composite at the 4/5 of the thickness and 1/3 and 2/3 of the length (Fig. 1). Vacuum bagging technique is basically an extension of the wet lay-up process where pressure is applied to the laminate once laid-up in order to improve its consolidation. A fiber content of about \( V_f \approx 20\% \) vol. was calculated using equation 2 after the determination of the density with equation 1. Bio-composites were further cured under vacuum for 8 h in an oven at the controlled temperature of \( T_c = 100 \, ^\circ\text{C} \) to limit the deterioration of flax fibers. Three different types of EP/FF bio-composites were fabricated to compare the influence of the FF reinforcement structure on mechanical properties: random orientation of flax fibers in mats, preferential orientation of flax fibers (in the direction of load) in a UD fabric taken as received and especially fabricated after selection and individualization of the fibrils according to a protocol developed by Coroller et al.

**Characterization techniques**

**Density measurements**

The density of composite samples has been determined with a METTLER-TOLEDO balance using equation 1 in order to evaluate the fiber volume fraction with equation 2.

\[
\rho_{\text{composite}} = \frac{m_{\text{air}}}{m_{\text{air}} - m_{\text{ethanol}}} (\rho_{\text{ethanol}} - \rho_{\text{air}}) + \rho_{\text{air}}
\]

Where \( \rho_{\text{composite}} \rho_{\text{ethanol}} = 0.789 \, \text{g cm}^{-3} \), \( \rho_{\text{air}} = 0.0012 \, \text{g cm}^{-3} \), are the densities (g cm\(^{-3}\)) of the sample, ethanol and air and \( m_{\text{air}} \), \( m_{\text{ethanol}} \) the mass of the composite sample in air and in ethanol (g) at room temperature.

\[
V_f(\%) = \frac{\rho_{\text{composite}} - \rho_{\text{epoxy}}}{\rho_{\text{flax}} - \rho_{\text{epoxy}}} \times 100
\]
Piezo-resistive measurements in static and cyclic modes

The piezo-resistive properties of quantum resistive strain sensors (sQRS), were investigated with a servo-hydraulic INSTRON 5566A tensile machine able to measure force and displacement during extension experiments. Tensile tests were done using a crosshead speed of \( V_c = 1 \text{ mm min}^{-1} \), at \( T = 23 \text{ °C} \), with RH = 50% relative humidity, in the longitudinal direction of fibers, within the linear deformation range of bio-composites. The load was measured with a 10 kN cell, and the strain with an axial extensometer of \( L_0 = 10 \text{ mm} \) nominal length. Cyclic tensile tests were performed at different deformations (crosshead displacement) with a data acquisition frequency of \( f_d = 5 \text{ Hz} \) and various cyclic programs. Incremental tests were composed of 5 levels of increasing/decreasing displacements in the range of strain \( 0.1\% < \varepsilon < 1.2\% \). In situ electrical measurements were performed with a HBM MX840A QUANTUM device in direct current (DC) at a monitoring voltage of 1 V.

Principle of sQRS

After connecting sQRS it was possible to investigate the evolution bio-composite’s health under known loadings by simultaneously recording the piezo-resistive responses of sQRS and the stress–strain trace from the extensometer. The strain sensing ability of sQRS results from their conducting architecture made of percolated nanofillers, very sensitive to any variation of the average interparticular gap. In such network the electrons’ circulation is governed by the Ohm’s law in the quiescent state and switches progressively to Zener tunneling under strain. Therefore, \( A \), the electrical response of sQRS expressed by equation 3 can strongly increase due to the exponential variation of the tunneling conduction (second term) that overwhelms the linear evolution of the ohmic conduction (first term) as expressed in equation 4, reported
Results and discussion

Morphology of smart bio-composites

The sensitive network of CNT former within the poly(epoxy) electrically insulated matrix allows to monitor the structural health of the FF/EP bio-composite wherever sQRS are disposed. However, before analyzing sQRS electrical signals, it is important to characterize the morphologies of the smart material at the different scales of observation. Fig. 2 shows SEM and TEM imaging of the different steps of fabrication of sQRS made by spraying 20–30 layers of CPC solution directly on flax fibers’ surface during the composite samples’ processing, to obtain 1.5–2-μm thick sensitive films of $R_0 = 0.5–10$ MΩ (depending on batches) integrated at the interface between FF and EP. Fig. 2a clearly shows the non-homogeneous nature of a single CPC layer, which contains many pores of 10–40 μm diameter. The holes result from the quick evaporation of the solvent (chloroform in this case) during the CPC solution drying. Although such porous structure could be looked for in the design of vapor transducers (vQRS) to increase the exchange area between analytes and carbon network, here pores are considered as defects that could initiate crazes. It is thus necessary to make sure that these holes will be filled during the layer-by-layer process; from Fig. 2b it seems to be the case as the surface appears smooth after only five sprayed layers. Fig. 2c is a SEM fractography of the cross section of a EP/FF sample that gives a good idea of FF distribution within the EP matrix and reveals also the complexity of interfaces. The tiny area between FF and EP where the sQRS is implanted cannot be easily analyzed by SEM, but TEM reveals well its presence in Fig. 2d. Therefore, the final thickness measurement allows to deduce that single layers are about 50–100 nm thick.

by Tjong et al. to be universal and applicable to percolating carbon filler based nanocomposites.

$$A_e = \frac{R - R_0}{R_0}$$  \hspace{1cm} (3)

where $R$ represents the resistance of CPC sensors under strain and $R_0$ the quiescent initial resistance.

$$j(E) = \sigma E + AE^\alpha e^{-B/E}$$  \hspace{1cm} (4)$$

where $j$ (A cm$^2$) is the current density, $E$ (V cm$^{-1}$) represents the electric field per distance unit, $A$ is proportional to the tunneling frequency, i.e. the number of attempts per second made by the carrier to cross the barrier, $\alpha$ is a critical exponent, $B$ is a measure of the energy barrier between the insulating matrix and the filler material, and is therefore proportional to the gap width between nanofillers.

Another interesting characteristic can be derived from sQRS piezo-resistive responses, such as their sensitivity to strain, which can be evaluated experimentally by calculating the slope of the resistance versus strain curve in the elastic domain (first area in the electrical response), which further can be expressed through the gauge factor (GF) according to equation 5.

$$GF = \frac{R - R_0}{R_0} \frac{L - L_0}{L_0} = A_e/\varepsilon$$  \hspace{1cm} (5)$$

where $R_e$ and $R$ (Ω) are the resistances, $L_e$ and $L$ (m) are the lengths of the sample, respectively, before and after load, $A_e$ and $\varepsilon$ is the deformation.

Moreover, these experiments are meaningful to quantify the damage accumulation, step by step during tensile tests, by the analysis of both mechanical and electrical properties.
Mechanical properties of bio-composites

Flax fibers have almost the same mechanical performances as glass fibers when reported to their density, but present the advantage of a much lower environmental impact, due to their bio-based and biodegradable nature. Nevertheless, as typically observed flax fibers present a non-linear behavior at low strain (under $\varepsilon = 0.2\%$), unlike their glass homologues which do not go through any change in modulus in the same range of deformation. Fig. 3 illustrates the influence of the reinforcement structure, i.e. random orientation of FF for the mat, preferential orientation in the direction of load for UD. As expected, the two UD composite samples perform better than the mat one for approximately the same fiber volume content ($V_f = 20.1 \pm 1.0\%$), with Young’s moduli about 3 to 4 times larger, and despite a 10% smaller strain at break. Moreover, comparing the UD microcomposite made with selected FF to the standard UD composite made with the commercial FF fabric shows that a proper selection, separation and individualization of FF into elementary microfibrils, before impregnation with EP, brings over 25% of improvement in mechanical properties as already pointed out. Nevertheless, in the following as no particular gain in mechanical properties was looked for, all UD composites were fabricated with the commercial fabric more easy to process.

Monitoring the mechanical behavior of poly(epoxy)/flax fibers UD composites with sQRS

Strain monitoring of EP/FF with embedded sQRS in static mode

The typical piezo-resistive behavior of poly(epoxy)/flax fiber UD composites under quasi-static tensile loading was investigated by recording simultaneously their stress/strain plot and relative resistance response of sQRS. Among all sensors produced according to the protocol reported in the experimental part, only 50% were active once connected, and the results presented here correspond to a selection of the most representative traces that have been obtained: Sensors 0a and b were disposed symmetrically according to Fig. 1 to examine the reproducibility of their piezo-resistive response upon monotonic loading (Fig. 4). Sensor 1 was used alone and disposed in the middle of the sample to compare the shape of its piezo-resistive response to that of the testing machine during loading/unloading cycling up to failure (Fig. 5a). Sensors 2 and 3 were disposed symmetrically to check the reproducibility of signals upon incremental strain up to failure (Fig. 5b). The main characteristics of the five embedded sensors used in the following are collected in Table 1.

Table 1 demonstrates that sensors having comparable $R_0$ (of some MΩ), introduced in composites with sections comprising quite the same number of bundles (in average 2800 per 0.1 mm²), can have rather different gage factors GF depending on their mechanical history and location in the sample. The micromechanical behavior of EP/FF is complex as flax fibers have a multiscale structure: Fibers are composed of fibrils gathered in bundles of one to three dozen cells that encircle the vascular cylinder. The bundle cohesion is insured by pectins, accumulating in the primary wall and cell junctions. Hence, it is thus possible to introduce sQRS in the core of bio-composites to monitor strain but also to learn more about the micromechanical behavior of composites as described in Fig. 4. At first sight both mechanical and electrical signals have a monotonous evolution. It can be noticed that the two sensors 0a and 0b have almost the same response with a curvature opposite to that of the mechanical trace. This demonstrates the good reproducibility of samples’ fabrication because their symmetrical disposition with respect to the center of the composite sample makes that they must be exposed to almost the same deformation. The loss of linearity observed over $\varepsilon \# 0.2\%$ of strain is due to the onset of the damage mechanism typical of flax fiber-based epoxy composites.

In the first step of deformation, i.e. below $\varepsilon \# 0.2\%$ of strain, there is an almost linear relationship between the applied stress and the electrical response that makes it possible to calculate GF. Depending on the level of strain the gauge factor is comprised between 3.75 and 10 ± 1 (Table 1), which is a two to five times larger value than that of classical metallic gauges for which very often GF # 2. Interestingly, the end of the purely elastic behavior zone can be detected by the change of slope of the $A_r$ curve, which makes it possible eventually to anticipate the bio-composite’s degradation simply by monitoring the sQRS signal. In the second step of deformation, from $\varepsilon \# 0.2$–0.4%, $A_r$ increases non-linearly, until $\varepsilon \# 0.4\%$ where it recovers a linear evolution. The strength of sQRS is that their macroscopic piezo-resistive response originates from the nanoscale, where tiny variations of the average inter-nanofiller distance change the ratio between quantum tunneling and classical ohmic conduction. When tunneling takes advantage on ohmic conduction, the resistance increases exponentially according to equation 4 as presented above, and this makes CPC very sensitive to mechanical solicitations. Hence, any movement of less than ten nanometers due to macro-molecular relaxation or craze propagation can be transduced into an electrical response provided that this happens in the vicinity of the nanotubes’ network.
The strain upon the first loading, it does not come back to its initial value after unloading. This could come only from the sensor itself, but this non-reversible effect is also detected on the mechanical trace, thus confirming that the structure of the material as changed during the test and that the sensor was able to follow it. Moreover, from the second to the fourth cycle, both the electrical and the mechanical responses are perfectly matching (between $\varepsilon = 0.2$ and $0.8\%$) until the breakage over a deformation of $\varepsilon = 1.2\%$ during the fifth and final cycle. It is likely that the mechanisms implied in the modification of the composites’ initial Young modulus ($E$) and sensors’ gauge resistivity ($R_0$) are responsible for the observed behavior.

**Figure 4** Typical stress/strain and piezo-resistive trace monitored by sensors 0 a and b of epoxy/flax fibers UD composite ($V_f = 22.1 \pm 0.5$)

**Figure 5** Evolution of $A_r$ and strain of bio-composite samples with time during (a) Monotonous loading/unloading cycling over the elastic limit (0.2%) monitored by sensor 1, (b) Incremental loading/unloading cycling under and over the elastic limit monitored by sensors 2 and 3

**Table 1** Main characteristics of sQRS instrumented EP/FF UD composite samples

| Samples                  | Sensor 0 a/b | Sensor 1 | Sensor 2 | Sensor 3 |
|--------------------------|--------------|----------|----------|----------|
| Fibers’ volume fraction: $V_f$ (% vol.) | 22.1 ± 0.5   | 20.1 ± 0.5 | 13.6 ± 0.5 | 13.4 ± 0.4 |
| Bundles per 0.1 mm² (>1200 μm²) | 48 ± 5       | 48 ± 5   | 54 ± 5   | 51 ± 5   |
| Size of bundles μm²          | 2820 ± 100   | 2880 ± 100 | 2780 ± 100 | 2720 ± 100 |
| Initial resistance: $R_0$ (MΩ) | 2.2/3.6   | 6.4      | 1.5      | 0.8      |
| GF (σ0.5) in linear domains [σ] | 3.75 [0–0.2%] | 9.5 [0.3–0.5] (1st load), 10 [0.35–0.5%] (2nd,3rd,4th loads) | 3 (1st load), 4 (2nd,3rd,4th loads) | 3 (1st load), 4 (2nd,3rd loads) |

**Strain monitoring of EP/FF with embedded sQRS in cyclic mode**

A further investigation of the piezo-resistive behavior of sQRS instrumented EP/FF UD composites has been conducted by submitting composite samples to different tensile loading/unloading cycles (Fig. 5) in order to characterize the appearance of nonlinear phenomena in their mechanical behavior.

In Fig. 5a, samples have been stretched up to 0.8%, which is four times the value previously identified as their elastic limit in static mode. This experiment obviously shows a first trend of damage: although the piezo-resistive response follows well the strain upon the first loading, it does not come back to its initial value after unloading. This could come only from the sensor itself, but this non-reversible effect is also detected on the mechanical trace, thus confirming that the structure of the material as changed during the test and that the sensor was able to follow it. Moreover, from the second to the fourth cycle, both the electrical and the mechanical responses are perfectly matching (between $\varepsilon = 0.2$ and $0.8\%$) until the breakage over a deformation of $\varepsilon = 1.2\%$ during the fifth and final cycle. It is likely that the mechanisms implied in the modification of the composites’ initial Young modulus ($E$) and sensors’ gauge resistivity ($R_0$) are responsible for the observed behavior.
factor (GF) at intermediate strain between $\varepsilon = 0.2$ and 0.35% of strain are related to the slippage of flax fibers in the bundles. Moreover, this demonstrates the ability of sQRS to sense deformations induced tiny structural changes in the composite above its elastic limit. To better understand this phenomenon, additional cyclic tests have been led with incremental loadings of 0.1, 0.3, 0.5, and 1% of strain, to investigate the differences between the elastic and non-elastic behaviors in EP/FF composites (Fig. 5b). Although sensors 2 and 3 have different initial resistances, $R_i = 1.5$ and 0.8 MΩ, respectively (Table 1), for similar fiber contents ($V_f \% = 13.5\%$), their GF is almost the same step by step. Actually, GF is changing from a cycle to the other as it is calculated from the average slope of the piezo-resistive signal. But a finer analysis shows that in reality from the third cycle, the signal’s curvature changes due to the appearance of an inflection. This trend is much more visible in the fourth and last cycle that leads to failure. Thus, the appearance of an inflection in the sQRS signal can be considered as a precursor sign of the composite’s failure, which could provide a way to anticipate breakage. The fact that this trend is observed on both sensors 2 and 3 is a confirmation that the phenomenon observed does not come from the sensors, but really from the composite material in which they are embedded. Moreover, Fig. 5b also shows that the ultimate phase is different for the two sensors, i.e. they don’t see exactly the same events during the breakage as the failure must be more or closer from sensor 3 than from sensor 2. However, although the two sensors did not have exactly the same experience, they are both able to predict the failure at the same time. Additionally, one can see that from a local information the global behavior could be to some extend anticipated. Given the importance of the curves’ slope to help understanding the piezo-resistive behavior of the bio-composite failure under loading/unloading cycling, we have examined the evolution of this parameter as a function of maximum strain and step in cycle. Fig. 6a summarizes the evolution of Young’s moduli $E$ (slope of stress/strain curves), respectively in the first and second linear part of the first loading ($E_{\text{1 elast/post}}$), and following loadings ($E_{\text{i elast/post average}}$). Fig. 6b collects in the same way the gauge factors $GF$ of the first and second linear part of the first loading ($GF_{\text{1 elast/post}}$) and following loadings ($GF_{\text{i elast/post average}}$) by analyzing the slopes’ changes in the electrical response as a function of strain. The first trend of Fig. 6a is that $E$ is not changing much with the maximum strain, whereas a more important decrease in slope is observed for the first cycle ($−40\%$) than for the four following ones ($−20\%$). Moreover, it can be noticed that under the elastic limit (here for $\varepsilon = 0.1$) there is no difference of slope, $E_{\text{1 elast # 1 post}}$ and $E_{\text{i elast # i post}}$. Fig. 6b shows the same features for GF as for $E$ but somehow amplified and of opposite sign: over $\varepsilon = 0.1$ the deformation is leading to non-reversible structural changes evidenced by more and more important increase in GF over this limit as the maximum strain is increased. This effect is always more marked in the first cycle than in the following ones, meaning that the damage is not accumulating provided that the maximum amplitude of deformation is kept constant.

All these results demonstrate the ability of sQRS to probe mechanical properties’ evolution in the core of the composite, in particular by following the history of their gauge factor.

**Conclusion**

A simple approach to embed carbon nanotube-based conductive polymer nanocomposite sensors inside unidirectional flax fibers – epoxy composite samples has been investigated. The quantum resistive strain sensors were built in situ by spray layer by layer during the bio-composite’s fabrication. They have demonstrated their versatility and effectiveness in the monitoring of damage taking place in bio-composite samples during static and dynamic cycling, with strains levels of different amplitudes, under and above the elastic limit. sQRS have demonstrated their superiority on classical metallic gauges that can only monitor strain under the elastic limit and only on samples surface. Additionally, sQRS can be five times more sensitive and also detect the appearance of non-reversible damage before the complete failure of the composite. From this point of view, it is especially interesting to monitor the evolution of sensors’ gauge factors changes that can inform about the composite’s health. Moreover, sQRS are also less sensitive to corrosion and moisture and do not need any intermediate glue to transfer the load. Our findings could open the way to a larger development of more secured bio-composites with embedded strain sensors.

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