Interfacial nanocomposite sensors (sQRS) for the core monitoring of polymer composites’ fatigue and damage analysis

Suvam Nag-Chowdhury\textsuperscript{a,b}, Hervé Bellégou\textsuperscript{a}, Isabelle Pillin\textsuperscript{a}, Mickaël Castro\textsuperscript{a}, Pascal Longrais\textsuperscript{b} and Jean-François Feller\textsuperscript{a}\textsuperscript{c}

\textsuperscript{a}Smart Plastics Group, Bretagne Loire University (UBL), IRDL CNRS 6027 – UBS, Lorient, France; \textsuperscript{b}ESI Group, Rungis, France

ABSTRACT
The quick development of the smart factory and prognostic and health management (PHM), in the fields of aeronautic, automotive and green energies, is evidencing a need for sensors able to monitor the behavior of composite materials all along their life at the closest of the matter. In situ fabricated conductive polymer nanocomposite (CPC) sensors are bringing an interesting solution to this prospect as they can be integrated homogeneously in the core of composites to probe their deformations and damage. In particular fatigue which is one important mode of failure of polymer composites can be monitored from early signs of damage until the final breakage by analyzing the piezo-resistive response of quantum resistive strain sensors (sQRS) made of carbon nanotubes. We have developed all these aspects in the paper taking the example of a classical glass fibers/epoxy composite instrumented in its core with two sQRS to monitor its short and long term fatigue behavior.

1. Introduction
In the prospect of future developments of concepts such as smart factory\textsuperscript{[1]} and prognostic and health management (PHM)\textsuperscript{[2]} many industries using polymer composites such as aeronautic, automobiles, ships, and green energies are looking for solutions of damage monitoring increasing systems’ reliability while reducing maintenance requirements. The tendency is to make these composite structures remain in operation for longer periods of time\textsuperscript{[3]} and expose them to increasingly harsh and complexity service environment\textsuperscript{[4]}. One important part of this chain is the implementation of damage detection and online monitoring strategies to extend the life of these engineering infrastructures. Thus, there is a need to develop sensors able to follow the behavior of composite materials all along their life at the closest of the matter\textsuperscript{[5]}.

Fatigue is a mechanism that occurs in most materials during their service life below the fracture strength and therefore it must be followed by a long-term structural health monitoring (SHM) process periodically updated and validating the ability of the operational structure thanks to a pertinent diagnostic. Due to their excellent specific strength-to-weight ratio and outstanding resistance to fatigue

CONTACT Jean-François Feller jean-francois.feller@univ-ubs.fr Smart Plastics Group, Bretagne Loire University (UBL), IRDL CNRS 6027 – UBS, Lorient, France

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damage, fiber-reinforced polymer composites (FRP) become superior over their metal analog. However, the failure of composite laminates is rather complex and is a combination of matrix cracking, delamination, and fiber breakage, which can reduce mechanical strength of the composite in contrast to their metallic counterpart [6,7]. Therefore, it is essential to implement sensors in composite structures to provide an early warning for damage evolution before their catastrophic failure. Different systems exist: acoustic emission (AE) allows the continuous monitoring of micro-structural degradation, residual stresses and fatigue damage in material but it does not allow strain monitoring in the absence of damage [8,9]. Ultrasonic inspection allows cracks detection, but it does not allow stress/strain sensing in real time [10,11]. Damage detection can be also be realized by a breakage of the optical fiber, resulting in a loss of a transmitted light signal [12] or by mechanical coupling, where a change in local strain leads to a change in the coefficient of refraction [13]. However, although fiber Bragg gratings (FBG) have been successfully embedded in composites [14], it has been pointed out experimentally and with finite element analysis that this could downgrade significantly the composite's ultimate tensile strength [15]. Other works mention that optical fibers could act as a notch in the composite material and therefore reduce the threshold for initiation of transverse cracking [16,17]. Actually, the diameter of optical fibers can be 20 times larger than that of reinforcement fibers and may lead to processing issues during their insertion between plies depending on the complexity of the part. This is why the investigation of advanced composites monitoring by piezo-resistive measurements, able to provide in situ sensing of both strain and damage has attracted much attention of the scientific community. Early works of Chung et al. [18,19] and Schulte et al. [20–21] report the monitoring of electrically conductive reinforced polymer composites’ damage using their constitutive carbon fibers. Classically, the strain sensing of electrically non-conductive composites is achieved by sticking metallic strain gages of gauge factor around 2, onto the surface of structures. However, they cannot monitor large deformations and failures, as they tend to be first detached before the complete destruction of the sample is reached [22].

Hence to completely monitor the health of composite structures it is necessary to develop a system able to monitor continuously both strain and damages at critical locations upon a wide spectrum of mechanical solicitations. By mimicking nature, i.e. human skin, the idea of intelligent materials (IM) and structures able to continuously ‘feel pain’ like the human neural network upon external solicitations such as stress, temperature, low and high frequency vibrations, is attractive [23]. This is why a significant amount of fundamental research has been performed to develop carbon nanotube-based strain sensors with stable and reliable electrical responses. Thostenson and Chou [24–28] made a pioneers’ work to develop and model the piezo-resistive behavior of glass fiber-reinforced composite samples with embedded in situ conductive carbon nanotube networks. Alternative approaches have been reported such as the incorporation of carbon nanotube (CNT) films, known as bucky paper [29,30], CNT/polymer films [31], CNT-coated polymer fibers [32,33], CNT fibers [34], Fuzzy fibers [35], electrostatic layer-by-layer (eLbL) multi-layered thin films [36,37], spray of a CNT network onto glass fibers [38]. Among all studies on strain monitoring of CNT-based composites, only a few of them concern the monitoring of fiber-reinforced polymer composites with carbon nanotube-based sensors to follow dynamic strain and fatigue damage, although there is still a great need for a method of fatigue damage detection that can be plausibly extended to real systems. One of the advantages of nanocomposite sensors is that they can either be stuck on the surface or embedded inside composite structures. Additionally, sensors such as conductive polymer nanocomposite (CPC) can be fabricated in situ during the processing of composites to be homogeneously integrated in their core and probe deformations and damage as shown in previous works [39,40].

But to go further, it is interesting to investigate in more details the fatigue, which is a very important mode of failure of composites, by instrumenting them with quantum resistive strain sensors (sQRS), to monitor their behavior from early signs of damage until the final breakage. It is exactly what we aimed in this work.

2. Experimental details
2.1. Materials
Carbon nanotubes NC-7000 MWNT (CNT) were kindly provided by Nanocyl (Belgium). This grade corresponds to multiwalled nanotubes with an average diameter of 10 nm and a mean length between 500 and 1000 nm. Epolam 2020 epoxy resin and amine hardener were purchased from AXSON, France. Chloroform (99%) was provided by Aldrich (France). Taffetas e-glass fiber (orientation of plies 0°/90°, surf. weight 165 gm.m−2) was purchased from Gazechim (France).

2.2. sQRS and CPC transducers’ fabrication
Calculated amounts of MWNT and epoxy resin were homogenized in chloroform by ultra-sonication
with a Branson 3510 sonicator for 90 min at 25°C, and further degassed for 5 min. After dispersion of CNT in epoxy resin, amine hardener (100:34 weight ratio of epoxy to hardener) was added and the mixture was further sonicated for 30 min. Then the sQRS were structured by spraying the CPC solution layer-by-layer (sLbL)\(^{[39-42]}\) either directly on glass fibers’ surface before the assembly of plies (interfacial core sensors), or after (sensing skins) as depicted in Figure 1 (right). The homemade spraying device visible in Figure 1 (left up) is allowing a precise control of the nozzle scanning speed \(V_s = 10\, \text{cm.s}^{-1}\), the solution flow rate \((50\, \text{mm.s}^{-1})\), the stream pressure \((p_s = 0.20\, \text{MPa})\), and the target to nozzle distance \((d = 8\, \text{cm})\). This allowed a good control of CPC transducers’ structuring.

### 2.3. Composites’ processing & instrumentation

After sensor in situ fabrication directly on glass fiber plies’ surface, these two electrically active layers were kept at top and bottom of other 16 layers of glass fiber and finally covered with two other layers in a vacuum bag. The infusion of the epoxy matrix was then performed at a pressure of \(p_i = 80\, \text{kPa}\). Finally, each sample contains two sensors just below two surfaces (top and bottom) as described in Figure 1. More details about the fabrication of sQRS can be found in our previous papers\(^{[40-42]}\). To monitor the deformation of the specimen and provide a reference (at least in the elastic domain) to compare with the responses of sQRS, a Kyowa KFGS-10-120-C1-11 metallic gauge composed of a CuNi alloy grid deposited on a poly(imide) foil with a resistance of 120 \(\Omega\), a length of 10 mm\(^2\) and a gauge factor \(GF = 2\), was glued onto the surface solicited in extension.

### 2.4. Characterization techniques

A Tecnai 20 transmission electron microscopy (TEM) operating at 200 kV was used to characterize the sensor and to determine the sensors’ thickness. An Instron 5566 servo-hydraulic test machine was used to measure force and displacement in static three-point bending test to measure flexural strength and flexural modulus of the host composite beam. Dynamic loading was provided by a servo-hydraulic Epsiflex from Prodemat (France) that also provided the displacement during measurement. Loading was repeatedly applied at a fixed stress amplitude (fixed mid span deflection). An incremental loading was applied to samples by progressively increasing the stress amplitude. Longitudinal strain data were measured by using a commercial strain gauge stuck on the test specimen. Dynamic 3-points flexural tests were performed at different frequencies, i.e. 5, 10, 15, 20, and 30 Hz. In situ electrical measurements were performed in direct current (DC) with
an additional Quantum HBM digital multimeter a monitoring voltage of 1V. Data were acquired at 100 Hz for in situ resistance measurements.

3. Results and discussion

3.1. Intrusiveness of sensors in static mode

A major concern with the introduction of any embedded sensor is the eventual weakening of the laminate composite it may generate. To investigate this fact, static three-point bending tests were performed on epoxy/glass fiber composites beads. Figure 2 shows the typical mechanical behavior of samples which main characteristics are collected in Table 1.

Figure 2 shows that the two composite samples with and without sensor have very similar mechanical characteristics. It can also be seen that, for both EP/FV samples used in this test, the elastic limit was reached for a deformation ($e_0$) of about 1%, meaning that over this value the materials is encountering non-reversible phenomena such as creep or damage. Table 1 evidences also that their Young’s modulus ($E_f = 20.7$ GPa), stress at break ($\sigma_b = 474$ (MPa)) and strain at break ($\epsilon_b = 3.25$ (%)) were actually almost identical and in good agreement with classical epoxy/glass fiber composites.

It clearly suggests that the introduction of a thin sQRS inside the composite must be non-intrusive and that the CPC film behaves the same as the epoxy resin of the matrix. This point will be discussed in the next paragraph. Additionally, the fractography in Figure 3 reveals the thickness of an interfacial sQRS coating the surface of a glass fiber, about 1.5 $\mu$m. These values are similar to those obtained by TEM in Figure 1.

Figure 3 also shows the tiny dimension of the CPC film, which is about 1/10th of reinforcing glass fiber’s diameter, and 1/100th that of the optical fiber used in composites for health monitoring.

3.2. Piezo-resistive response of sQRS under cyclic flexural loading

The three-point bending flexural test is logically soliciting the composite beam in extension on one of its side and compression on the other (see Figure 1 right). In order to demonstrate the efficiency of sQRS to monitor the mechanical behavior of composite beams in three-point bending mode under cyclic solicitations, two of them were embedded just under both surfaces, so that they will be loaded in tension and compression resulting in opposite piezo-resistive responses $A_r$ as defined by Equation 1.

$$A_r = R - R_0 / R_0$$

(1)

$A_r$ being the relative resistance amplitude or piezo-resistive response, $R$ the resistance upon loading and $R_0$ the initial resistance in quiescent conditions.

A sinusoidal flexural load of $F = 100 \pm 50$ N at $f = 10$ Hz was applied to the instrumented composite samples as described in Figure 1 (right). To have a reference at least in the elastic domain of deformation, a commercial metallic strain gauge was also stuck on the surface of the laminate specimen submitted to extension during the fatigue experiment. Figure 4(a,b) describe the piezo-resistive responses ($A_r$) of the two sQRS under cyclic bending, respectively when the sQRS is on the same side as the metallic gauge and on the opposite side. As it can be seen in these figures, the strain is alternating between $\epsilon = 0.44\%$ and $\epsilon = 0.68\%$, which corresponds to a strain maximum amplitude of about $\pm 0.12\%$ centered on 0.55% (corresponding to the preload), i.e. under the elastic limit of $\epsilon_e \approx 1\%$ previously determined from Figure 2 in static mode.

As expected, the resistance of the sQRS inserted in the compression side (Figure 4(b)) decreases upon flexural loading (leading to a negative $A_r$, i.e. negative strain coefficient NSC), whereas the sQRS exposed to extension (Figure 4(a)) sees its resistance increase with loading (resulting in a positive $A_r$, i.e. positive strain coefficient PSC). Whereas no visible variation in the piezo-resistive response ($A_r$) amplitude was observed during the initial step of fatigue, it was found to gradually increase together with the decrease in stiffness of the composite specimens.

| Three-point bending test | Flexural Modulus $E_f$ (GPa) | Flexural Stress at break $\sigma_b$ (MPa) | Flexural Strain at break $\epsilon_b$ (%) |
|--------------------------|-------------------------------|---------------------------------|---------------------------------|
| Without sensor           | 20.9 ± 0.5                    | 472.0 ± 5.2                    | 3.30 ± 0.1                      |
| With sensor              | 20.4 ± 0.8                    | 476.1 ± 7.4                   | 3.23 ± 0.2                      |
observed in both sides submitted to tension and compression. However, the increase of amplitude of $A_r$ was larger in the tension surface than compression surface. In this context the sensing mechanism of quantum tunneling resistive strain sensors (sQRS) can be explained by assuming that the variation of the average distance between CNT at junctions in the percolated network, is resulting in an exponential change in the quantum tunneling resistance according to Equation 2. However, although this model explains well the increasing difficulty of electrons to jump from a nanotube to the other across a potential barrier when the distance between them increases, it must be kept in mind that the separation distance $s'$ in Equation 2 is less than 20 nm. This means that tiny modifications of both macromolecules and nanotubes' conformations can be recorded but also that over a critical value of $s'$ the circulation of carriers will be switched.

Moreover, as the deformation of the CNT network reflects more generally that of the whole composite and in particular that of the matrix in which it is embedded, any non-reversible deformation will result in a permanent drift in resistance that can thus be considered as a damage marker.

$$\frac{R}{R_0} = [1 + e^i]e^{(s-s_0)}$$ (Equation 2)

With $R$ and $R_0$ respectively the initial resistances upon loading and in quiescent conditions, $e$ the deformation of the sample, $s$ and $s_0$ respectively the inter-particular distances upon loading and in quiescent condition, $\gamma$ is defined by Equation 3.

$$\gamma = \frac{4\pi(2m\phi)^{0.5}}{h}$$ (Equation 3)

With $\phi$ the height of potential barrier between adjacent particles for epoxy about 0.5 to 2.5 eV, $m$ is the electron mass and $h$ the Planck's constant.

Consequently, at the beginning of the fatigue test no permanent resistance drift is expected whereas over a large number of loading/unloading cycles or by increasing the load, any debonding of the fiber/matrix interface, creep of macromolecules or fibers' breakage, will affect permanently the sQRS integrity and basal resistance. The resulting non-reversible modifications of the average inter-particular distance between the nanotubes at conductive junctions in a more or less important part of the percolated network will thus induce an exponential variation of the global resistance of the sQRS and allow to track the degradation of the composites' mechanical properties. Inversely to what happens on the extension side, upon constant loading on the compression side, there is a decrease of CNT-CNT distance according to what was also observed in papers on carbon fiber self-sensing composites. This results in a densification of the CNT network leading to a resistance drop. Consequently, the simple monitoring of the evolution of $A_r$ on both sides of the specimen in tension and compression, can provide precious indications on the level of microscopic damage accumulation in the composite.

### 3.3. Strain monitoring with sQRS

To evaluate the effect of the stress level (expressed by the load ratio ($L_r$) defined in Equation 4), on the piezo-resistive response of sQRS ($A_r$), the specimen were mechanically solicited at 10 Hz in Epsiflex Prodemat using a data acquisition frequency of 100 Hz with a minimum constant load of $F_{\text{min}} = 50$ N.

$$L_r = \frac{F_{\text{min}}}{F_{\text{max}}}$$ (Equation 4)

With $F_{\text{max}}$ and $F_{\text{nom}}$ respectively the maximum and the nominal load applied to the specimen.

The maximum load $F_{\text{max}}$ was increased from 100, to 192 and then to 313 N, whereas the corresponding $A_r$ were simultaneously recorded. Figure 5 shows the evolution of piezo-resistive response of the sQRS for different load ratios, $L_r = 0.50, 0.26,$ and 0.166 calculated with Equation 4. It is observed that the decrease in the load ratio $L_r$ is followed by an almost linear increase in the amplitude of $A_r$, as attested by Figure 5 (inset). Moreover, the sQRS appear to have a fast dynamic as they are able to follow the deformation even for low load ratios, which correspond to faster strain speeds. In fact, it

![Figure 4. Piezo-resistive responses vs time of the sQRS $A_r$ red curve (lower amplitude, right scale) and the metallic gauge (strain blue curve (larger amplitude, left scale)) to sinusoidal stress at $f = 10$ Hz on the side: (a) in tension, (b) in compression.](image-url)
is also likely that the faster/larger the solicitation the greater the fatigue damage, hence the larger the probability for irreversible residual strain/resistance as it will be seen in the following. This is a first demonstration of the effectiveness of embedded sQRS, to monitor the stress magnitude in the composite sample by continuous in situ measurements of $A_r$ with a simple approach.

By extending this concept to real industrial cases, sQRS could be widely deployed in composite parts and embedded in critical locations (where overloads or stress concentrations are expected) to perform in situ real-time monitoring of their deformation. This would thus provide a tool to probe the strain level in the overall structure that could significantly improve safety and reliability of composites in many industrial sectors using ever increasing fractions of these materials such as aeronautic, green energy, automotive, and naval, by monitor the stress/strain levels continuously in ever more challenging structures. Moreover, a good understanding of the real stress/strain levels in the core of the composite at critical locations identified by a simulation of the structure performances, will also help the design engineers to optimize the sizing of parts by a finer modelling of structural components’ mechanical behavior.

To go further in the sQRS capability validation, it is important to check their ability to detect quick transitions in stress/strain evolution that could be precursor signs of damage initiation during long time fatigue solicitation.

### 3.4. Response of frequency sweep test

Before investigating the damage of composites with embedded sQRS it is interesting to verify the effect of the solicitation frequency on their $A_r$ in order to eventually evidence asynchronic behaviors (uncoupling of mechanical and electrical signals) and optimized the fatigue test conditions. To do so, the response of sQRS ($A_r$) has been overlaid to the signal measured by a commercial metallic gauge (strain) stuck on the surface of the specimen in extension, under a sinusoidal stress solicitation upon decreasing/increasing frequencies. The results are displayed in Figure 6.

The load level applied to obtain the results of Figure 6 is only 20% of the load generating the ultimate fracture of the composite that was determined in static conditions (Table 1), so that no micro-cracks are expected to be initiated in such conditions. From Figure 6 it can be seen that the sQRS give an instantaneous and clean response closely fitting that of the strain gauge. At first glance it can be seen that the frequency sweep is not affecting this correlation even at relatively high loading frequencies. Thus, it was decided that $f=10$ Hz would be the preferred frequency of solicitation for composite beam when possible. However, in Figure 6 some differences in amplitude between the traces of the two kinds of sensors are visible, which is not so surprising as they don’t have exactly the same location (the sQRS is inserted in the core between plies and the commercial gauge is stuck on the surface of the specimen) nor the same nature (the sQRS is almost chemically homogenous with the composites’ matrix, whereas the metallic gauge must be glued, introducing two additional interfaces and is heterogeneous by nature). Nevertheless, the amplitude of both signals is found to decrease during the incremental frequency sweep, and to increase during the decremental frequency sweep, which may be ascribed to the viscoelastic behavior of the composite’s matrix less able to comply at higher speeds of deformation. Actually, this behavior may not be associated with a polarization effect that would otherwise have been observed in both ways. Finally, this experiment has shown that whatever the frequency was, both the sensors were
able to monitor synchronically deformation when the cyclic solicitations were not expected to damage the specimen. Despite their introduction in the core of samples, sQRS do seem to give reliable and repeatable responses which encourage their use for longer time fatigue tests in order to get closer to structural health monitoring (SHM) requirements for real applications.

3.5. Structural health monitoring of composite beams

Fatigue behavior is generally of great interest in the composite field as the repetition of non-critical stresses, or at the contrary punctual overloads can trigger the initiation of microcracking that can lead to ultimate failure of the structure in a way difficult to predict. There are several illustrations of such fractures in racing sailing boat masts or in wind turbine blades that unfortunately often could not be avoided. In order to examine the ability of sQRS to monitor the evolution of long-term performances of composites samples, dynamic measurements were done during fatigue loading of the composites beams submitted to \( \varepsilon = 1.40 \pm 0.15\% \), that is, over the elastic limit, at \( f = 10 \text{ Hz} \) during 2.5 days. Figure 7 shows the piezoresistive responses of the sQRS \( (A_r) \) and metallic gauge (strain) on the side in extension (a) Strain larger amplitude left scale, (b) \( A_r \) large amplitude, right scale.

Figure 6. sQRS responses ‘\( A_r \)’ and metallic gauge ‘strain’ measured with time for a sweep of frequencies: (a) increasing from 2 Hz to 20 Hz, (b) decreasing from 20 Hz to 2 Hz.

Figure 7. Response to a strain solicitation \( \varepsilon = 1.40 \pm 0.15\% \) at \( f = 10 \text{ Hz} \), of sQRS \( (A_r) \) and metallic gauge (strain) on the side in extension (a) Strain larger amplitude left scale, (b) \( A_r \) large amplitude, right scale.
The sQRS resistance increment during fatigue experiments can be associated to a decrease in stiffness of both the composite and the nanocomposite, expected to have similar ageing, revealing non-reversible phenomena such as creep, delamination, fibers’ fracture etc. A comparison of the differences between maxima and minima of $A_r$ in Figure 7(a,b) reflects almost no evolution in the short-term (less than 0.6%) but significant changes in the long-term as fatigue proceeds (about 20%). Therefore, to push ahead the long-term sensitivity of sQRS to fatigue, a new test was performed at a deformation even more above elastic limit of the composites, that is, $\varepsilon = 1.6\%$, during 5 days at a frequency of $f = 10$ Hz, the piezo-resistive response being continuously monitored by a Quantum HBM.

Figure 8 gives a new insight in the visualization and quantification of the damage accumulation through the monitoring of $A_r$, features’ evolution such as non-linear shape and amplitude increase. It is now very clear that $A_r$ has lost its linearity after a long time continuous evolution. In the beginning of the fatigue test the piezo-resistive signal is reproducible upon dynamic loading/unloading cycles, although the composite is progressively losing its stiffness (as already seen in Figure 7). But in a next step of fatigue, after 40 M cycles, another kind of non-reversible phenomenon is taking place, certainly due to larger damages in the composite samples as evidenced by discontinuities in the transducer’s response $A_r$ (supplementary peaks). These results demonstrate the ability of sQRS to follow the accumulation of different kinds of damages resulting from fatigue, such as polymer relaxation, fiber debonding or pull-out and breakage, although these events are difficult to identify individually. Nevertheless, in a previous work the use of acoustic emission (AE) had allowed to confirm that cracks could be associated to singular events in the $A_r$ trace, thus it is likely that after a training period a finer identification will be possible\cite{40}. Moreover, Figure 8 suggests that the new peaks appearing in the $A_r$ curves indicate that the sQRS is keeping the memory from a cycle to the other, of the non-reversible deformations and damages that can result from the continuous tensile and compression loadings inducing in particular micro displacements of glass fibers perpendicularly to the mechanical solicitations. This finding shows promise in the use of sQRS to provide early warning of composites’ damage evolution during fatigue before their catastrophic failure.

Figure 9 provides another interesting angle for damage growth analysis, by representing the relative load loss ($F_{\text{max}}/F_{\text{0max}}$) of the composite beam instrumented with one sQRS on its extension face under dynamic bending at $f = 10$ Hz during a fatigue test of 3 M cycles.

![Figure 8. Piezo-resistive response of the sQRS inserted in the side of the specimen ($A_r$) submitted to $\varepsilon = 1.6\%$ in extension at $f = 10$ Hz during 40 M cycle (5 days).](image8)

![Figure 9. Compared evolution of $A_r$ and load decrease $F_{\text{max}}/F_{\text{0max}}$ of an FV/EP composite beam instrumented with one sQRS on its extension face under dynamic bending at $f = 10$ Hz during 40 M cycle.](image9)
Development. Damage mechanisms in cross-ply composite laminates have been studied for decades and are also following the same kind of sequence from crack initiation, transverse crack in the plies normal to the applied loading direction, delamination at the interface of plies to fiber breakage at ultimate fracture as pointed out by Vadlamudi et al.\cite{50} Quaresimin et al.\cite{51} and Dzenis \cite{52}. The same stages of damage growth are evidenced in Figure 9, as both curves of relative load loss $F_{\text{max}}/F_{\text{max}}$ and sQRS piezo-resistive response $A_r$ versus the logarithm of the number of cycles, reveal the presence of three, or more steps during the damage growth.

In Figure 9, the first step (I) is characterized by a slight drift in $A_r$ until approximately 0.7 M cycles, which corresponds to the early stage of fatigue, indicating no strong damage in the composite but yet some relaxations in the epoxy matrix or at the interface. Over this point, the stage (II) is marked by a significant increase in $A_r$, well synchronized with a franc decrease in the force necessary to maintain the deformation, indicating the occurrence of enough significant damage to decrease the apparent stiffness. Subsequently, over 1.1 M cycles, in the stage (III) the damage is maintained by fatigue crack propagation, namely the formation of transverse cracks in the 90° plies, until complete saturation and delamination at the interface of layers. The accumulation and interaction of multiple damage mechanisms is responsible for the sharp increase of resistance change in the last stage, which results in ply delamination between the 0° and 90° layers. Delamination continues to grow and accumulate until glass fiber failure occurs at 2.7 M cycles.

Thus, although the composite sample’s fracture is not announced by a sudden change in either the mechanical or the electrical trace, this experiment demonstrates the possibility to instrument composites with sQRS to monitor their fatigue and trigger eventually the unloading or maintenance of the structure once $A_r$ will have reached, for instance 80% of its value at the fracture.

Moreover, in contrast with Figure 8 which was allowing to evidence only punctual damages (breakages, opening and closing of micro cracks) taking place in the composite during its fatigue, through the appearance of supplementary peaks and changes of slope in $A_r$ plot, the following of the evolution of $A_r$ on the long-term is allowing to assess the level of damage of the composite.

4. Conclusion

Fabricating conductive polymer nanocomposite (CPC) transducers’ in situ onto glass fiber plies by spray layer by layer (sLbL) at the interface with the epoxy matrix, was shown to open a novel approach to monitor the health of polymer composites. The high sensitivity of the so-called quantum resistive strain sensor (sQRS) to structural changes in composites, is mainly resulting from the effective strain transfer from the epoxy matrix or the glass fibers to the sQRS, due to its homogenous nature and hierarchical conductive architecture. Thus, the conducting network of the nanocomposite proved to be very effective to sense either small reversible deformations or keep the memory of non-reversible structural modifications during fatigue. The cyclic loading tests also demonstrated that the piezo-resistive response $A_r$ of sQRS can provide several temporal indications of damage, punctually by exhibiting supplementary peaks and slope change in $A_r$ during loading/unloading but also globally by evidencing different damage regimes from the slope variation of $A_r$ amplitude with time, until the composite’s fracture. Therefore, if sQRS are widely deployed in a whole structure, they will be an efficient tool to probe the strain level and damage in different area of interest, which should significantly improve composite’s safety and reliability in many industrial sectors such as aeronautic, green energy, automotive, and naval. Moreover, a good understanding of the real stress/strain levels in the core of the composite at some locations necessary to validate the predictions made by simulation softwares, will also help the design engineers to optimize the design of parts by a finer modelling of structural components’ mechanical behavior.

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Notes on contributors

Suvam Nag Chowdhury is currently Manager Materials Specialist at Bajaj Electricals Ltd, Mumbai. He got his master degree from Indian Institute of Technology Delhi, and then obtained his PhD in a joint collaboration between University of South Brittany & ESI group, France in 2014. He has worked on the development of conductive nanocomposite strain sensors for the validation of simulation of damage, and published three papers in scientific journals.

Hervé Bellegou is assistant engineer specialized in the development of electronic devices for the acquisition of
data from any kind of experimental devices since 1996 at IRDL CNRS Lab. In particular he has worked on the design of experiments to characterize both piezo- and chemo-resistive properties of conductive polymer nanocomposites (CPC).

Dr. Isabelle Pillin is engineer. She obtained her Ph.D. in 2001 on the study of the modification of the kinetics of crystallization of poly(butylene terephthalate) in the presence of additives such as dyes that can act as nucleating agents. Since then she has taken part to several research programs dedicated to characterization and development of polymer composites.

Dr. Mickael Castro obtained his Ph.D. in Polymer and Composites Materials from the University of Saint-Etienne (France) in 2004, studying the morphology and the rheological behavior of co-continuous immiscible polymer blends. During his post-doctorate at the University of Minnesota (USA), he studied the rheology of concentrated surfactant systems. Then he joined the Laboratory of Materials Engineering of Brittany (LIMATB) in the Smart Plastics Group in 2006 as a post-doc researcher and became assistant professor in 2009. His current research includes the development of Conductive Polymer nanocomposites to obtain intelligent materials combining multi-sensitivity to environmental changes.

Pascal Longrais is currently Visual Platform Product Line Manager at ESI Group, France. He obtained his diploma from Ecole Supérieure des Techniques Aéronautiques et de Construction Automobile (ESTACA) in 1987. Since 1997, he works in ESI group which develops an extensive suite of coherent, industry-oriented applications to realistically simulate a product’s behavior during testing, to fine-tune manufacturing processes in accordance with desired product performance, and to evaluate the environment’s impact on performance.

Prof. Jean-François Feller is a Professor specialized in “Physical-Chemistry of Polymers nanoComposites” at the University of South Brittany (UBS) in Lorient (France) since 2004 and is currently head of the Smart Plastics Group. He obtained his engineer diploma in “Plastics Engineering” at ITECH (Institute of Tex- tiles & Chemistry) in Lyon (France) in 1991. His Ph.D. (1995) at the University Claude Bernard of Lyon1 concerned the synthesis and characterization of coupling agents to control and tailor the glass fiber/poly(propylene) interphase in thermoplastic composites. His post-doctorate at IN2P3, Lyon, focused on the analysis of polymer coupling agents onto glass surfaces using the Particle induced Desorption Mass Spectroscopy (PDMS) technique. In 1996 he obtained an assistant Professor position at the University of South Brittany in Lorient where he has been interested in several research topics related to the development of Smart Plastics from conductive polymer nanocomposites (CPC) for temperature, strain and vapor sensing, to develop self-regulating heating devices, e-noses for anticipated diagnosis of diseases and gages for structural health monitoring of composites.

ORCID
Jean-François Feller http://orcid.org/0000-0003-2000-4247

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