ON THE WAY TO SMART BI-REINFORCED COMPOSITES TAKING ADVANTAGE OF RECENT ADVANCES OF NANOMATERIALS AND NANOTECHNOLOGIES ...

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Keywords : Smart Composites, Optical Fiber Sensors (OFS), durability, carbon nanotubes

Abstract

Smart composites with embedded sensors are an alternative concept to conventional methods based on externally-bonded sensors to structures' techniques. Many types of sensors can be embedded within composites, so that the behavior of composite structures under various stress sollicitations can be finely monitored. The first part of this work is a summary of some results obtained when using optical fibers as sensors, both as Fiber-Bragg-Gratings (FBG) as well as Rayleigh sensors. Stepping back to the nano level and due to their exceptional mechanical properties and their low density, carbon nanotubes are ideal fillers for the mechanical reinforcement of polymeric matrices. When properly dispersed, literature reports that a small amount of carbon nanotubes is able to enhance the mechanical behavior of thermosetting matrices. In this work, some results showing the beneficial effect of reinforcing thermosetting polymers with CNTs are presented. Creep under micro-indentation tests show a significant first stage creep on CNTs-reinforced resins which is increasing with the increase of CNTs weight's ratio. These promising results are opening new opportunities of bi-reinforcing polymers with continuous fibers as well as with small weight fraction of CNTs and some preliminary results are summarized.

1. Introduction

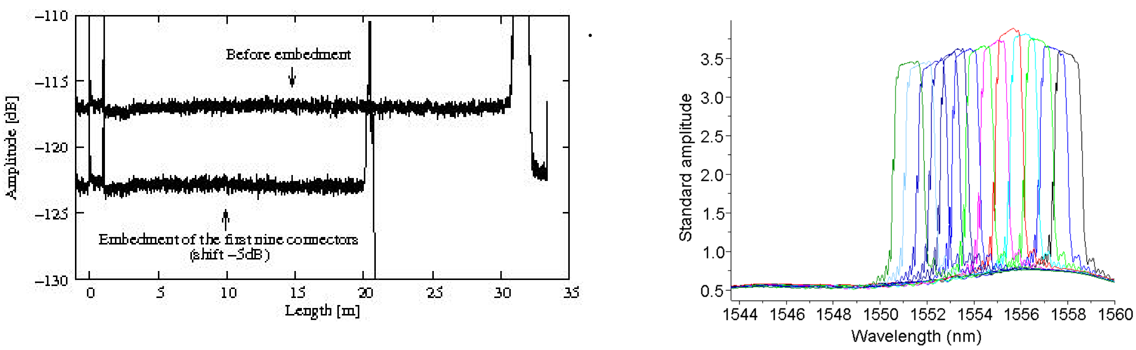
Polymer matrix composites are increasingly used as structures in various industrial fields. Their good mechanical properties, excellent corrosion-resistance, their rigidity/weight ratio higher than steels, their good processability and ease of installation are their main advantages. However, despite these advantages, some issues remain regarding mainly their sustainability and mechanical performance over the long term. It is therefore of a prime importance to develop suitable and reliable structural health monitoring techniques that will enable fine estimates of strain in various localizations and this concept is called smart composite. The instrumented composite structures are currently used in industrial applications, particularly in the aerospace sector. The coupling between the composite material "host" and an ongoing monitoring system health allows, in principle, getting information on the state of deformation and damage mechanisms that are emerging or being spread. The ultimate goal is to be able to suspend the use when needed and eventually to start maintenance in a timely manner. Conceptually, several techniques can be applied. These are based on conventional NDT techniques and have generated some success. Nevertheless, there are shortcomings which require the current research. This is the case, in particular, of the inability of a single NDT technique, to learn about all the pathologies of a structure, which led to the concept of data fusion. Moreover, the difficulty of interpreting and processing the signals received, for example by acoustic emission technique. The concept of embedded sensors in the heart of composites is offered to other application areas for which the possibility of obtaining information from the sensors as an integral part of the material is very appealing. Among the systems tested and put into practice, there are sensors based on fiber optics. This concept has attracted interesting progress through the development of Fiber-Bragg-Gratings that are currently the subject of intense research. Notwithstanding, many issues remain to deepen and this is for example, the case posed by the physical presence of the fiber material in the composites, in absolute terms, a defect in the mechanical sense. Moreover, for this type of sensor, location, positioning, loading configuration and the physical and mechanical integrity after fatigue tests, for example, are all issues still unresolved and deserve an extra effort supported.

Parallel to the above, and in some demanding industrial applications such as off-shore wind turbines, high speed transportation, there is a need for higher performance than what is exhibited up to date. During the last 2 decades, significant advances in the field of nanomaterials (strengthening of polymer matrices by carbon nanotubes, graphenes ...) and nanotechnology were recorded. It seems therefore natural to try to set-up bi-reinforced (with continuous carbon fibers and carbon nanotubes) composites materials.

This work is a short summary of what we have being doing so far in the field of smart composites and bi-reinforced composites.

2. Results & Discussions

Optical fiber sensors (OFS) better fulfill the requirements of embedded sensors in composite materials than piezoelectric sensors. They offer a good thermal resistance and a high mechanical strength, especially under tension, which prevents them from being damaged during the manufacturing process. Morevover, thanks to their very small size (diameter less than 250µm), they do not compromise significantly the structural integrity of composite materials ([5], [6]). The French Project Decid2 aims to build a 20m x 7m demonstrator made out of smart composite material that use fiber optic sensors. The smart composites are processed by pultrusion. The optical fiber used as strain sensors provides a structural health diagnosis *in-situ* and in real time. The platform DECID2 is intended to be sought outdoor, in fatigue and creep under low stresses (well below the end of proportionality). Some examples of results obtained within this project are presented. Optical fiber sensors are used to monitor continuously the process of pultrusion using Optical Backscattering Reflectometer (OBR).



Figures 1. (a) OBR tracking showing both a successfully embedded optical fiber as well as a failed one during pultrusion; (b) : Standard amplitude of FBG as a function the wavelength during load/unload cycling of a smart composite specimen.

Fiber-Bragg-Gratings (FBG) were also used to monitor strain during quasi-static and fatigue loadings under 3-point-bending. In both cases, results show that these sensors are performing very well and that reliable results can be obtained. A FBG is photo-inscribed grating in the core of the optical fiber with a given pitch. At each fiber Bragg grating corresponds to a Bragg wavelength. When there is thermal expansion or deformation of the fiber, the Bragg wavelength is modified. By studying the shift of the wavelengths, strain can be measured. It is also possible to multiplex an optical fiber with more Bragg gratings whose wavelengths of Bragg are sufficiently separated ($\lambda_B = 2 . n_{eff} . \Lambda$,Where λ_B the Bragg wavelength, n_{eff} the effective refractive index of the optical fiber and Λ the grating pitch). Optical fiber sensors were used at 2-step levels, during pultrusion, to check whether optical fibers were successfully pultruded within composite profiles and further to monitor strain during mechanical testing. One should keep in mind that not only optical fibers are introduced, but also the associated connections. The over-thickness that derives can be significantly hindered during pultrusion. Therefore, using an optical backscattering reflectometer (OBR), broken optical fibers can easily be detected. Figure 1a shows the signals before and after embedment of an optical fiber into a pultruded profile that show that the optical sensor has not experienced any damage and was positively inserted. On the reverse, when an optical fiber is broken, the OBR is a perfect indicator (Figure 1a), where the failure of the optical fiber is clearly shown. Embedded Fiber-Bragg Gratings (FBG) were used to get the deformation trigged during quasi-static flexure loading, as well. Figure 1b shows FBG standard amplitude as a function of the wavelength. This result shows clearly that there is an increase of the wavelength (thus, the strain) when increasing the load. Figure 2 shows the strain recorded by both FBG and mechanical testing machine. To enable an easy comparison between the two signals, a lag phase was introduced. As shown on the Figure, the strain measured using FBG is smaller than the one displayed by the mechanical testing machine. This is simply the result of the difference between the strain measured by the mechanical testing machine at the extreme of the area under tension and the position of the optical fiber inserted into the heart of the area under tension, but closer to the neutral axis. To get a match between the 2 signals, it is of a prime importance to run some additional mechanical calculation that help to figure out the accurate position of the FBG.

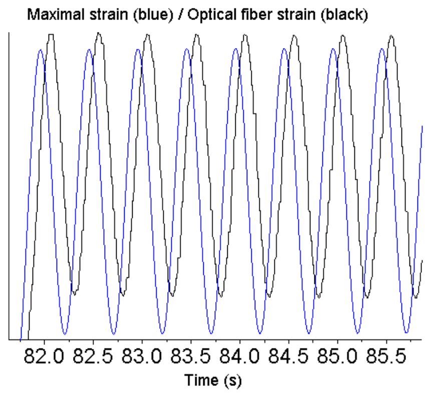
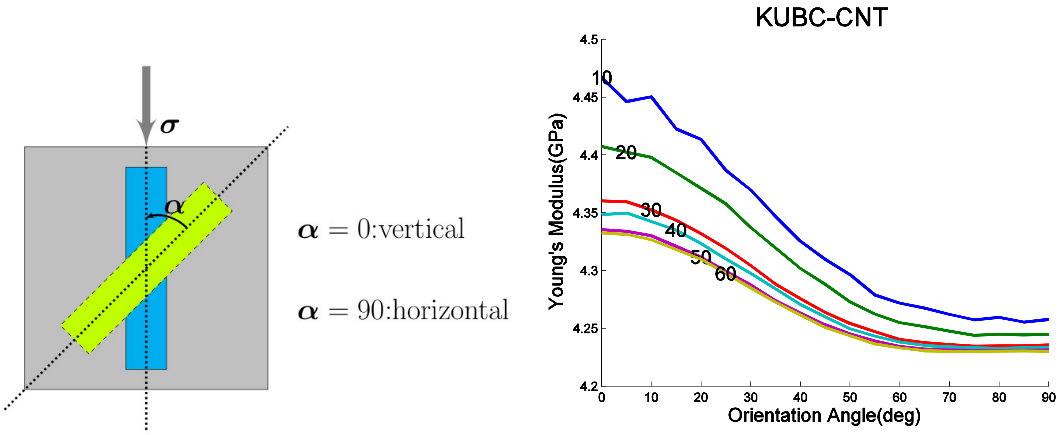


Figure 2. Comparison of strain values delivered by FBG and the mechanical testing machine.

Carbon nanotubes (CNTs) are good candidates for polymer reinforcement as they exhibit excellent mechanical properties (Young's modulus as high as 1TPa) and a very low density (1.8 g/cm^3). If correctly dispersed in the matrix, a small fraction in weight is able to enhance the stiffness of the polymer. However, the issue of dispersion of CNTs within resins is widely discussed in the literature. It has been shown that large fractions of CNTs are harder to disperse correctly in the matrix. Thus, for both, providing ease of processing as well as for obvious technological targets, only the results related to small weight fractions of CNTs were adopted and presented in this work.

In order to get a clear idea about the nanoreinforcement mechanisms induced by carbon nanotubes, the effort was put first on *ab-initio* modelling. This was conducted starting from of a nanocell of thermosetting polymer reinforced with a 1%wt. carbon nanotube. The calculations were conducted so that the effects of the orientation of the CNT regarding the compressive applied stress is studied. The interface CNT-polymer is assumed to behave viscoelastic, the CNT is assumed to behave elastic. Maxwell model is used to evaluate the viscoelastic behavior. The homogenization method with the Effective Interface Model was used to calculate the elastic Young's Modulus of the Nano-Reinforced composite. It is clearly shown from Figure 4b that the elastic Young's Modulus of the composite decreases with the increase of the orientation angle. The stress-strain curve was also properly simulated and showed that the bridging effect of the CNT is more efficient when the angle is increasing from 0° to 90°.



(a) (b)

Figures 4. (a) The nanocell considered showing the orientation angle of the CNT vs. the compressive applied load; (b) The Young's modulus values plotted as a function of the orientation angle

CNTs' Pull-out was observed under the Scanning Electron Microscope (SEM) as shown in Figures 5. This mechanism is a proof of existence of a reinforcing effect induced by the addition of CNTs to the matrix. Some aggregates of carbon nanotubes were also observed as shown in Figure 5b. Indeed, as reported in the literature, it is pretty tough to get large effective dispersion of carbon nanotubes.

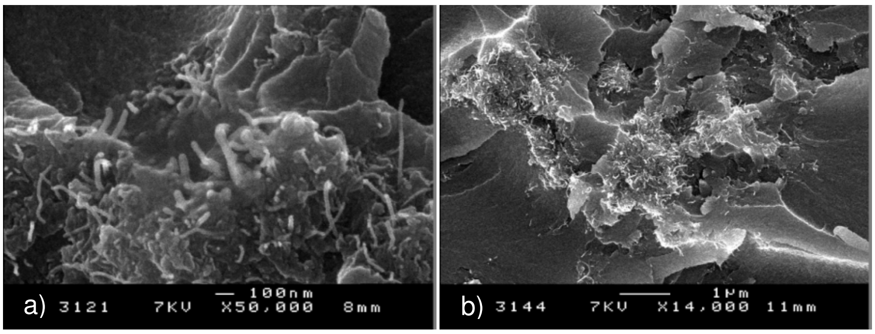


Figure 5. Carbon nanotubes dispersed in a vinyl ester matrix a) pull-outs, b) limited dispersion of CNTs

To evaluate the impact of reinforcement by CNTs, creep under instrumented micro-indentation technique was carried out and the shear creep compliances were measured. In the case of a linear elastic homogenous material, the relation of Sneddon (1965) [1] is establishing the link between the applied load, P_e, and the indentation depth, h, at the time, t.

$$h^n(t) = \frac{1-\nu}{\mu} \times F \times P_e(t) \tag{1}$$

Where μ is the shear modulus, ν the Poisson's ratio, F and n are constant values related to the tip geometry. In the case of viscoelastic materials, the elastic parameters μ and ν have to be replaced by their viscoelastic time-dependant counterpart υ and G, which is possible in the case of a monotonic increase of the area of contact. Lee and Radok (1960) [2] achieved this substitution using the method of functional equations.

$$h^n(t) = \frac{1-\upsilon}{F} \times \int_0^t J(t-s) \frac{\partial P(s)}{\partial s} ds \tag{2}$$

Where J is a Laplace-Carson transform of the creep shear compliance and υ a constant as the shear flow is incompressible and predominant at large time. We will take υ=0.5. The creep indentation loading is given by the step loading relation :

$$P(t) = P_0 H(t) \tag{3}$$

Where H is the Heaviside function, so expression (6) becomes

$$h^n(t) = \frac{1-\upsilon}{F} P_0 \times \int_0^t J(t-s)\,ds \tag{4}$$

And

$$J(t) = \frac{F}{1-\upsilon} P_0 h^n(t) \tag{5}$$

In the case of a cylindrical flat-punch, of radius a, the parameters of this equation are: F = 4a and n = 1. The shear compliance J can be decomposed into an elastic component $J_e = 1/\mu$ and a time-dependent component J_v, this latter corresponding to the viscoelastic contribution (viscous flow and delayed elasticity):

$$J(t) = J_e + J_v(t) \tag{6}$$

During an indentation-creep test, the elastic component, J_e, can be measured during the loading phase, if the indentation machine is calibrated; and J_v during the creep, without any calibration, as the load is constant. The creep under microindentation set-up was developed by [3] and [4]. The load, applied using a piezoelectric actuator, is ranging between 0.01 and 50 N.

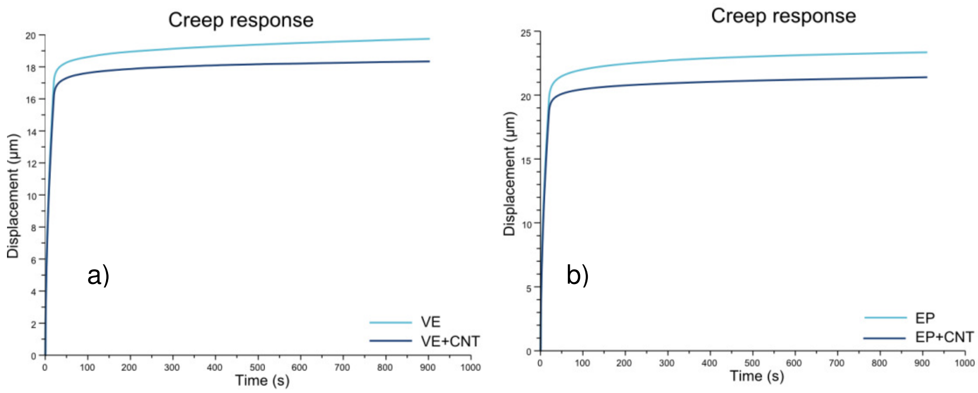


Figure 6. Indentation creep response curves of monolithic and nano-reinforced a) vinyl ester and b) epoxy resins

Figures 6 shows 15 minutes micro-indentation creep curves for monolithic and reinforced vinylester and epoxy resins. A change in the viscoelastic behavior is observed when comparing the monolithic and CNTs-reinforced matrice behaviors. This can be related to a stiffening mechanism of the matrix induced by the presence of CNTs. In the case of the epoxy resin, a significant decrease as high as 14% is even recorded for the viscoelastic coefficient for the reinforced matrix.

When conducting 50 hours creep tests, the primary creep stage is clearly highlighted for CNTs-reinforced resins. Moreover, the higher is the weight ratio of CNTs, the larger is the primary creep stage (Figure 7).

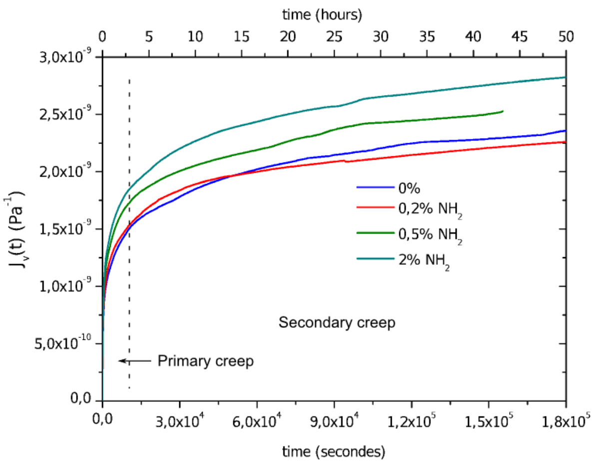


Figure 7. 50h shear creep compliance of neat and nano-reinforced epoxy

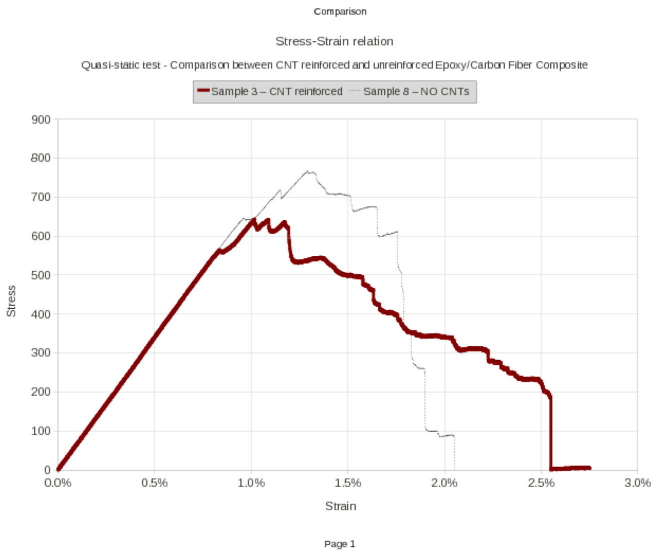


Figure 8. Stress-Strain curves of mono-reinforced and bi-reinforced epoxy matrix composites.

Based on the promising results of CNTs-reinforced composites summarized above, few trials were carried out so that a bi-reinforcement of epoxy matrix can be achieved through the addition of continuous carbon fibers as well as a small weight percent of CNTs. These trials led to specimens in rather good shape except that an amount of porosity was also recorded. The porosity is resulting from the high viscosity of CNTs-reinforced resin following the presence of carbon nanotubes. The comparative stress-strain curves under 3-point bending for both carbon fiber-reinforced epoxy and bi-reinforced (by both carbon fiber and carbon nanotubes) reinforced epoxy are displayed in Figure 8. There is no obvious effect of bi-reinforcement on the stiffness of since the Young's modulus calculated is 73GPa. On the reverse, a slightly higher value is recorded for the peak stress of the continuous carbon fiber-reinforced epoxy composite which is simply the consequence of the porosity of bi-reinforced one. The significant difference is the much larger non linear behavior recorded beyond the peak stress for bi-reinforced composite which is a proof that the addition of CNTs is leading to larger damage development, thus enhancing the resistance of the composite. Ongoing research is focusing on lowering the amount of porosity through the some process trials using liquid infusion. It is believed that mastering the porosity will significantly improve the overall mechanical behavior of bi-reinforced composites.

3. Conclusions

In this work, optical fiber-based sensors were used at during pultrusion to check whether optical fibers were successfully inserted within composite profiles. FBG were also used to monitor strain during quasi-static and fatigue loading. For both cases, this study showed very positive results about the insertion of optical fiber in a composite beam: no ruptures of the fibers during the pultrusion of fiber strength, low intrusivity and good reliability at high strained composites.

The reinforcement mechanisms following the addition of small weight ratios of CNTs to resins were evidenced. Carbon nanotubes pull-outs were observed through SEM observations. Micro-indentation creep tests show an increase in the viscoelastic coefficient as high as 14% for CNTs-reinforced resins. In addition, a primary creep stage was clearly displayed by reinforced resins, for which the higher is the CNTs weight ratio, the larger is the primary creep stage. This is a clear indication of the reinforcement through the addition of CNTs.

Preliminary trials to set-up reliable bi-reinforced composite materials (reinforced by continuous fibers as well as by carbon nanotubes) showed promising results. An extensive non linear behavior was recorded beyond the proportional limit, though a slightly lower maximum strength is recorded in comparison with carbon-fiber-reinforced resin. It is believed that this is due to the effects of porosity and ongoing research is currently focused on lowering it as an attempt of enhancing the overall mechanical behavior.

Acknowledgements

This work reports results from The National Project DECID2, funded by the French Government and The Area Pays de La Loire as well as a project supported by The Direction Générale de l'Armement (DGA) and The Carnot-VITRES Institute. MDH wishes to thank these organisms for the financial support.

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