Cure Monitoring and SHM of Carbon Fiber Reinforced Polymer Part II : Multi-Physical Correlations

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PART II : MULTI-PHYSICAL CORRELATIONS

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ABSTRACT

This article concerns the on-line monitoring of the manufacturing of composite materials using an ad-hoc instrumentation (based on electrical impedance measurements) considering the material it-self as a sensor. The material (made of T700 carbon /M21 epoxy prepegs) is here used as a sensor but could be also used as an actuator. Furthermore the instrumentation was developed to stay in the heart of the structure for SHM purpose. It is proposed to measure the changes in the electrical impedance of the composite material during curing. The changes of the resistance R_p and the capacitance C_p during curing are then correlated to rheological parameters linked to the progress of the curing reaction. The present paper exposes the estimation of electrical and rheological properties of the material using the measurements of R_p according to a specific curing cycle.

KEYWORDS :*Electrical properties, Multiphysical parameters, Process monitoring, Cure, SHM*

INTRODUCTION

Optimization of curing process and structural health monitoring (SHM) are of great importance in aeronautics for optimizing composite properties [1] and for safety reasons, respectively. Different strategies are encountered to monitor during curing the mechanical, thermal[2], rheological and electric behaviors [3] of composite materials using various types of sensors. But those rarely consider the material itself as a sensor and rarely keep the same sensors for SHM purpose.
The present paper deals with the in-line monitoring of the manufacturing of composite materials. This should provide reductions in process and material costs (number of required tests, curing time, reduced mass) and improve the properties of the manufactured composite structures. Here the instrumentation will remain inside the composite material for SHM purpose and also to ensure its functionalization. Specific thin flexible electrodes were inserted in the heart of unidirectional composite samples. Electrical impedance measurements were then undertaken and results highlight their correlation to the changes in thermo-mechanical and physic-chemical parameters during curing [4].The embedding of the electrodes in the heart of the material enables sensitive measurements of both resistance (*Rp*) and capacitance (*Cp*) satisfying the standard electric behavior [5]. The electrical resistivity of CFRP composites depends on the type and the orientation of the fiber and on the volume ratios of fiber, matrix and porosity [6]. It varies between 10^{-3} and 10^{-5}S/m in the direction of the fibers, and between 10^{-1} and 10^{-2}S/m in the transverse direction [7]**.** When the plies are stacked, contacts between fibers of adjacent plies are established, giving rise to a cross- plies resisvity highly linked to the quantity of resin and porosity between plies [7].Through the fibers, the longitudinal resistivity can be explained by the rule of mixtures[8]. The transverse resistivity can be determined by the percolation model taking into account the electrically ineffective length δ_{ec} [9].

However, the electrical resistivity through the thickness of laminates is calculated as the sum of the resistivity of plies and inter-plies (between plies)[7].
The electrical behavior of composites depends on multi-physical parameters such as:

- Rheological parameters (degree of cureα, dynamic viscosity, complex moduli, etc.)
- Geometrical parameters (the fiber, matrix and void volume ratios V_f, V_m and V_0 respectively, the number of fibers N_f, the percolation network and the effective cross sections)
- Electrical parameters (conductivity or resistivity, permittivity)

To ensure a real-time automatic control of the manufacturing the proposed electric model must take into account not only those physical parameters and the associated multi-physical laws but also the potential effect of the used electrodes (figure 1). To this end, experimental approaches were developed and different laws were established to refine all these multi-physical parameters taking into account potential scale effects. This will enable us to create a Resistance and Capacitance model to estimate *Rp* and *Cp* during curing. Measured *Rp* and *Cp* would then be compared with these estimations and, in the case of a good correlation, an inverse model could be constructed for monitoring and hence optimizing the process and thus the material properties. In this study, we are interested in validating the electric resistivity behavior of the material during curing. Then, thanks to the relation between the electrical resistivity ρ and the resistance R_p, we have chosen to correlate the changes in the value of R_p during curing to those of the rheological parameters. Theorical and experimental investigations are currently undertaken for the capacitance behavior.

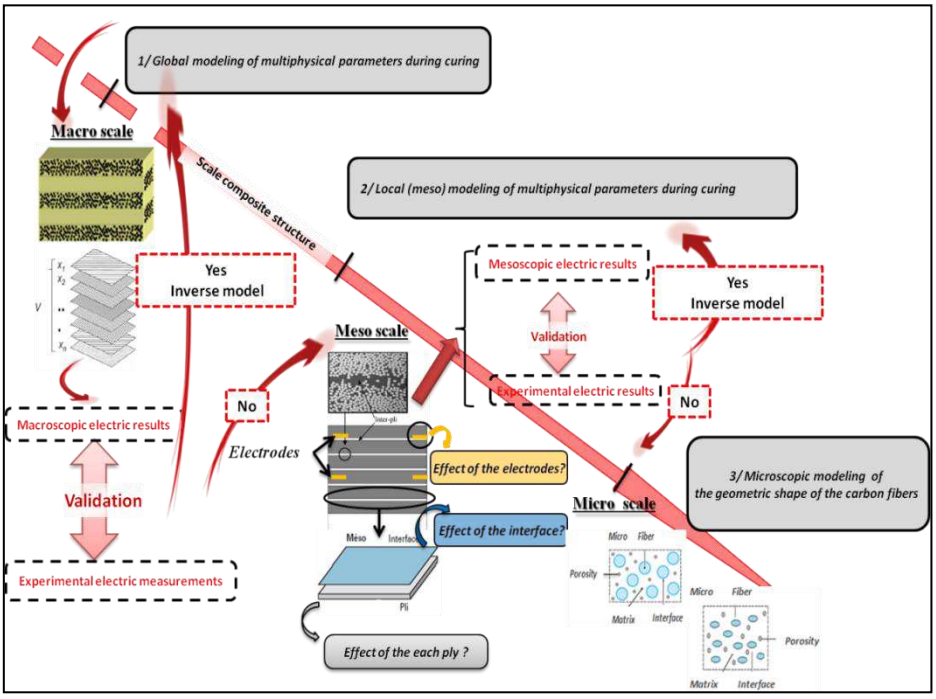


Figure 1: Strategy for identification of multi-physical parameters of T700/M21 composite

1 MATERIAL

Unidirectional composite samples made from Hexcel T700carbon/M21 epoxy prepegs (used in aeronautics and the space industry) are studied here. The thickness retained is 2 mm (8 plies).The resistance R_p and the capacitance C_p is extracted from the spectral response of the electrical impedance, respectively at low and high frequencies.
The electric conduction in a T700/M21 laminate can be described by two phenomena:

- a resistive conduction reflecting the electrical conduction through the fibers and the inter-fibers contacts points (percolation points) (figure 2): the higher the fiber rate, the lower the resistance value;
- a capacitive conduction reflecting the electrical conduction through the inter-fiber and inter-plies (via the resin): the capacitance can be affected by matrix and voids ratios.

2 EXPERIMENTAL PROTOCOL

Specific thin flexible electrodes (called flex) are inserted in the heart of unidirectional composite samples to minimize intrusiveness and ensure a low value of the contact resistance between the electrodes and the material.
As mentioned above, we are interested in studying the anisotropic electrical behavior of the composite material during curing. Different electrodes were placed transversally and longitudinally to the fibers to measure the longitudinal and transversal conductions of a single UD ply. For the electrical measurements through the thickness of the laminate, three flex were placed transversally to the fibers to measure the vertical conduction through the thickness and were inserted between plies 1 and 2 and between plies 7 and 8 of 100 mm x 100 mm samples.
Curing was carried out in an oven with a120-mn isothermal phase at 180 °C and with temperature rise and fall rates of 2 °C/min (cure cycle recommended by the manufacturer).
Our main objective is to provide evidence for correlation of the changes in rheological and electrical parameters during curing. To answer this issue, DSC and DMA analyses were undertaken to obtain the desired rheological parameters.

3 CORRELATION BETWEEN RP AND THE GEOMETRICAL PARAMETERS DURING CURING

A global (macro) study is not enough to monitor the geometrical, rheological and hence the electric behavior of the material during curing. Thus, it is appropriate to choose a meso-scale study taking into account the on-line distribution of these parameters through the composite structure (the plies and inter-plies).

3.1 LONGITUDINAL ELECTRICAL RESISTIVITY AND R_P OF T700/M21 DURING CURING

Figure 5 shows the estimated longitudinal resistivity by the rule of mixtures. About the estimation of this value, as a primary consideration, we suppose that the electric resistivities of the fiber and matrix are independent from the process parameters. As a secondary consideration, the longitudinal resistivity takes into account the influence of the temperature on the fibers [9] and the effect of the degree of cure α (we use here Maffezolli [10] and Pascault models [11]) on the electrical resistivity of the resin.

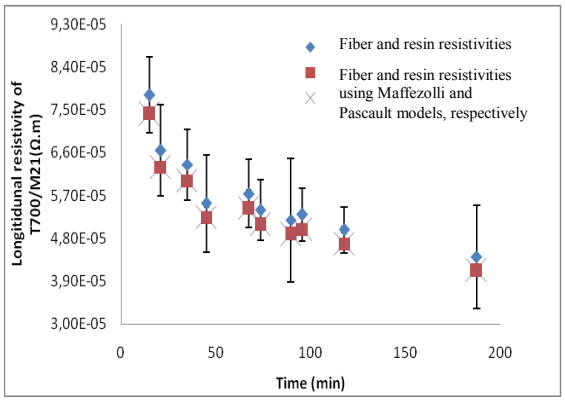
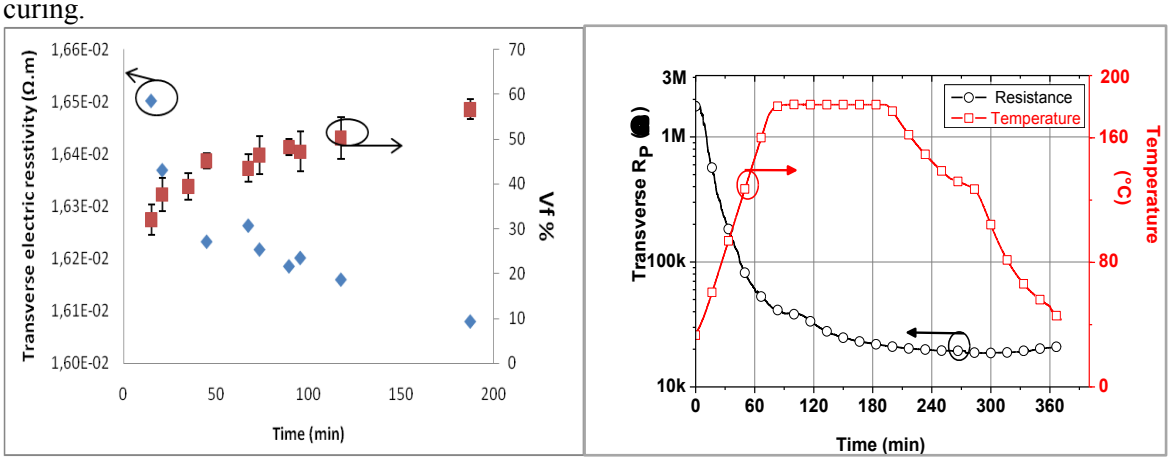


Figure 5: Longitudinal electrical resistivity predicted from the rule of mixtures during curing

The estimated resistivities obtained by the rule of mixtures are very similar to the data reported by [8] and [12], and this coincidence shows the validity of this law for the prediction of the longitudinal resistivity during curing. Also, it appears that the parameters of the curing cycle (temperature and alpha) have not a significant effect on the variation of the longitudinal electrical resistivity. Actually, it is difficult to identify the section of the electrical conduction in the fiber direction because it depends on the number of percolation points established between fibers. Thus, it is delicate to calculate the longitudinal resistivity from the measurements of R_p and hence it cannot be compared directly to the one estimated by the rules of mixtures. To ensure direct comparison (estimation-measurements), experimental approaches are currently undertaken to measure the number of the percolation points to estimate an average effective conduction area. Furthermore the values of the longitudinal measured R_p are affected by the contact resistance induced (by the amount of resin between the electrodes and the carbon fiber) exposing a higher value of the resistance as the one of the composite in the longitudinal conduction. Consequently, it will be not possible to monitor the curing process of our material using the electrical resistivity or R_p in the fiber direction. But as shown in [14] it could be used to monitor the temperature.

3.2 TRANSVERSE ELECTRICAL RESISTIVITY AND R_P OF T700/M21 DURING CURING

The knowledge of N_f and V_f (obtained by micro-structural analyses at different steps of curing) enables us to predict the electrical transverse resistivity of the composite. Here, we consider that the δ_{ecT} (electrically ineffective length in the transverse direction) is constant (δ_{ecT} =0.3mm [8] [9]) during the curing cycle. Figure6 shows the evolution of the transverse resistivity predicted from the percolation model (using microstructural analyses) and estimated from the values of R_p during curing.



(a) (b)

Figure 6: Transverse electrical resistivity: predicted from the percolation model (a)and measured using R_p values (b)

The changes in the estimated transverse resistivity is similar to this proposed by [8] on UD CFRP. This behavior is caused by the increase of the fiber contacts (percolation network), which is the main mechanism of the electrical conduction in the transverse direction [13]. The percolation model present higher values of the electrical transverse resistivity compared with these obtained in the fibers direction. From the electrical measurements of the transverse R_p it is delicate to estimate de corresponding resistivity because –as for the longitudinal case- it remains difficult to identify actually the section of the electrical conduction. As shown in Figure 6(b) the values of R_p are higher than the one of the electrode/ply contact resistance (about 1Ω). Thus this measurement can be used for the cure monitoring. Furthermore, it was shown that the resistive transverse conduction exhibits a good accuracy and a linear behavior with temperature and a high sensitivity to mechanical strain

[14]. Thus, the measurements of R_p through the transverse direction can also serve the functionalization of the material as a temperature and strain sensor.

3.3 R_P THROUGH THE THICKNESS OF T700/M21 DURING CURING

It is difficult to identify the section of the electrical conduction through the thickness because the path of this type of electrical conduction is unknown. It is strongly affected by the changes in the fiber, matrix and voids volume ratios not only in the plies but also in the inter-plies zones. Thus the changes in the value of R_p are used to characterize the electrical conduction through de thickness. Thanks to microstructural analyses and the measured values of R_p between 6 plies, estimated average values of R_p are given for each ply and inter-plies (figure 7).

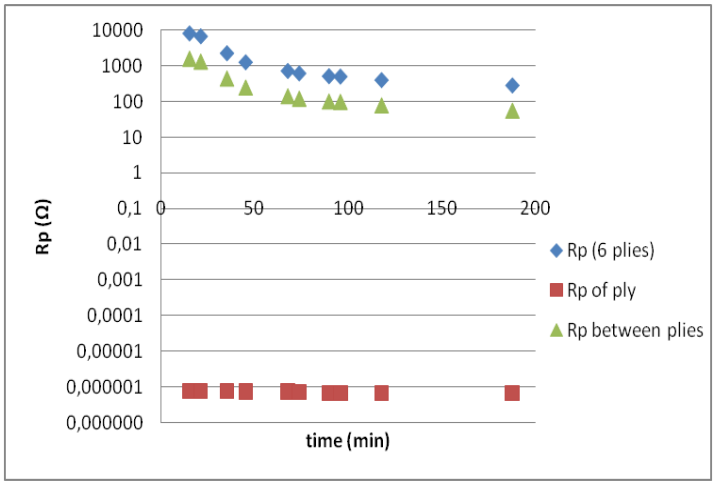


Figure 7: Electrical resistance through the thickness during curing

As expected, the electrical resistance in the thickness direction is strongly sensitive to the resistances of the inter-plies more than these of the plies. This behavior can be explained by the abrupt decrease of the fiber content and the increase of the resin-and-porosity contents between the plies as shown in the following figure:

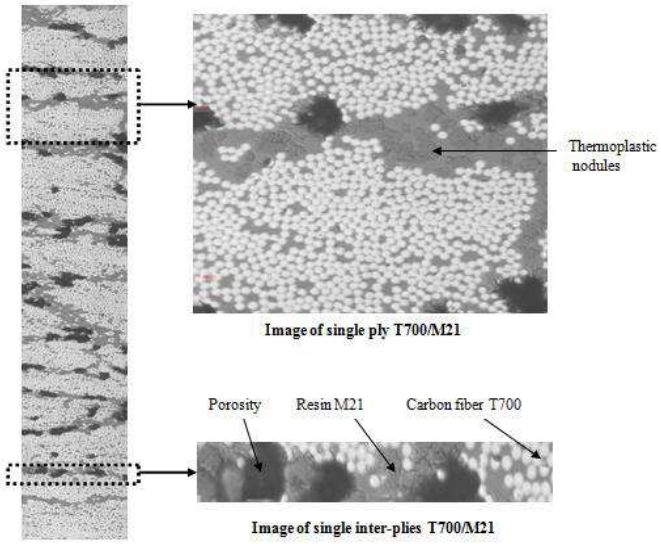


Figure 8: Images of thickness T700/M21 sample $[8]_0$

The measured values of R_p are sufficiently high to ensure a good sensitivity of the measurements through the thickness direction.

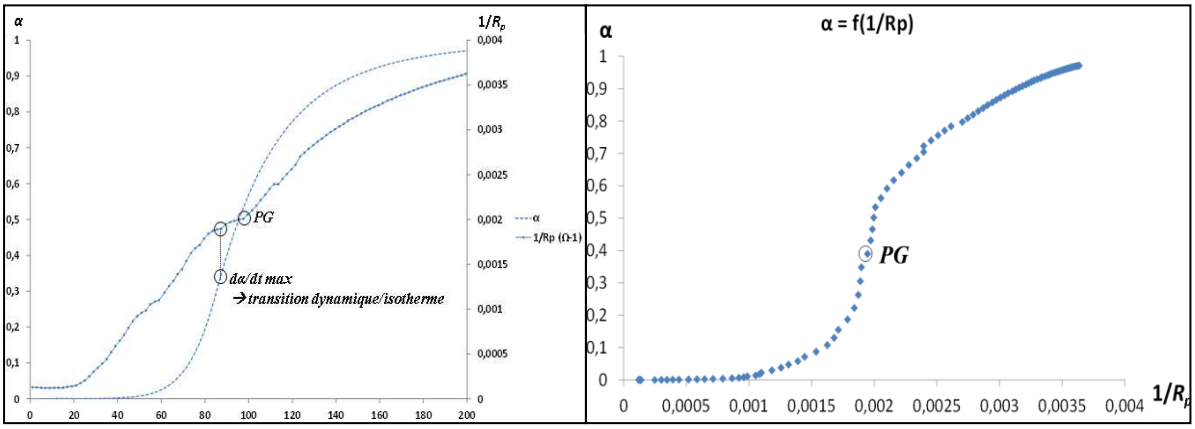
4 CORRELATION BETWEEN R_p AND THE RHEOLOGICAL PARAMETERS DURING CURING

From the obtained results, one can say that the use of the resistivity in the longitudinal and transverse conduction can't be used to ensure the monitoring of the curing process. Thus we will use the changes of R_p through the thickness for the purpose. To ensure an on-line automatic control of the manufacturing we have to define also multi-physical laws able de highlight the correlation between the electrical measurements and the rheological parameters.

4.1 R_p AND DEGREE OF CURE

Considerable works concerning the correlation between the electrical and rheological parameters have been made, and a number of studies have focused on the dependence of the electrical resistivity ρ on the degree of polymerization α during curing [10] [15].The main drawback of using the translation of the electrical resistivity signal to α,is the validation of this approach just under isothermal curing. Thus, we can over-come this limitation by the use of the measured R_p (through the thickness) to follow the evolution of the progress of reaction under both isothermal and dynamic curing conditions.

Figure 9 (a) shows a good correlation between the evolution of the degree of cure α (DSC determination) and the inverse of R_p versus the curing time.



(a) (b)

Figure 9: Degree of cure α and $1/R_p$ versus time of cure (a), prediction α from $1/R_p$(b)

As shown in the figure 9 (b), R_p shows two types of behavior for α which can be modeled before (power regression) and after the gel point *PG* (logarithmic regression). The correlation α-$1/R_p$ after the *PG* is in good agreement with this proposed by [10] and [15]. They are established a logarithmic correlation between the electrical resistivity and the degree of cure (samples made of pure matrix) under isothermal conditions.

4.2 CORRELATION BETWEEN R_p AND DYNAMIC MECHANICAL ANALYSIS

Very few techniques are available for monitoring the dynamic mechanical behavior of composite materials during curing. As described above, the degree of cure is highly linked to the R_p through the thickness of the material. On the other hand, the degree of cure is correlated to the changes in the viscosity μ of the thermoset resin during curing [16] . Furthermore, there is a linear relationship between the viscosity and the conservation modulus G'. This latter is strongly linked to the dissipative modulus G" [14]. Consequently, the measurements of R_p takes into account the changes of all the dynamic mechanical parameters of the material. It was shown in [4] that up to twelve rheological points (representative of the changes in the viscosity, the dynamic shear modulus, the loss tangent and the degree of cure) were detected using the electrical impedance approach during curing.Figure 10 exposes experimental laws linking the viscosity and the dissipation modulus to the

inverse of R_p. For μ and G'', global laws can't be defined as easily as for α. For example, local laws should be defined for each phase transition using the corresponding characteristic points.

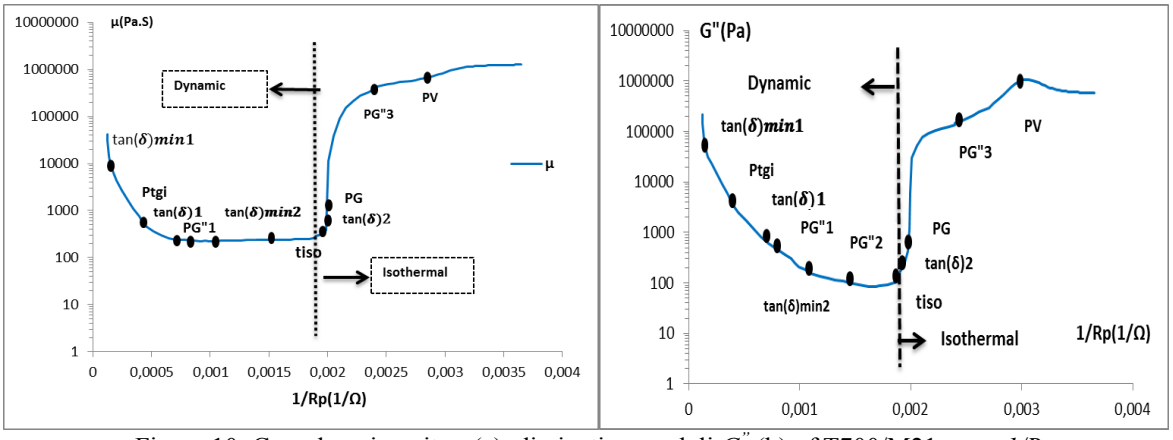


Figure 10: Complex viscosity μ (a), dissipation moduli G'' (b) of T700/M21.vs vs $1/R_p$

CONCLUSION

In the course of this study, we investigated the electrical anisotropic resistive conduction taking into account the variation of different multi-physical parameters during curing. It was found that the values of the longitudinal resistivity are too low to serve for the monitoring of the curing process but could be used to describe the thermal behavior of the material.

In the transverse and the through-thickness direction, R_p presents a sensitive behavior to the curing reaction. Thus they can be used to ensure the monitoring of the curing but also to describe the thermal and mechanical response of the material for functionalization and SHM purpose.

A current study focuses on the same approach to highlight the potential use of the capacitive conduction.

By modelling the rheological parameters, and equally the physical (fibre/resin and porosity rates) and thermal parameters through electrical impedance-metric values, it should be possible to establish in real time the appropriate moments for stopping, modulating or correcting the cure cycle. Looking beyond the manufacturing stage, electrodes at the heart of the material can also act as monitors of the health of the composite material during the conditioning stage and the service stage (SHM and functionalization of the material). A second type of modelling will be required to evaluate changes in the physicochemical and mechanical parameters that will come with aging or damage to the material.

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