CONTRIBUTION TO THE IMPROVEMENT OF SHIELDING EFFECTIVENESS OF COMPOSITE MATERIALS

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Abstract

This study shows the effect of the size and the carbon black morphology on the electric behavior of the thermosetting resin. Indeed the reduction of the size of carbon black granules in the matrix allows obtaining a weak percolation threshold and a significant improvement of electric conductivity. Also, it promotes the infiltration of the filled resin through the fibrous preform retaining the principle of infusion composite manufacturing. Finally the composite material with carbon black has a good electromagnetic shielding in comparison to the composite material without carbon black.

1. Introduction

In the industry of aeronautics, shipbuilding and military, the use of composite materials is constantly evolving because of their important mechanical performances and their low density. Also, these composite materials offer the possibility to integrate, during the manufacturing process, specific functions such as an electromagnetic shielding function and electrostatic discharge [1]. This is for example the case of the aeronautical structures where it is necessary to ensure a very high electric conductivity in order to facilitate the electric charges flow during lightning and to offer a screen against electromagnetic interferences. The integration of these functions by the improvement of the electrical conductivity allows avoiding structural damage by the breakdown and excessive rise of temperature. On the other hand, it protects the operation of embedded electronic systems against electromagnetic disturbances.

Usually, the composite structures which are used in the different domain described previously are generally composed of polymer thermosetting matrix reinforced with carbon or fiber glasses. This material presents a low electrical conductivity level due to the character insulating of polymer matrix. Authors presented different works [2, 3] where they are interested to incorporate electromagnetic shielding function in non-reinforced thermoplastic polymers. Some improvements of electromagnetic properties are carried out integrating conductive nano-fillers.

This work is devoted to characterize the shielding effectiveness of carbon black filled composite material reinforced with glass and carbon fibers. In the first step, the realization of the material is proposed using two processes of manufacturing namely infusion and RTM

Eco. In the second step, a measurement device is used to study the electromagnetic behavior of the realized material. Performances of shielding are obtained using a specific device developed by H. Vasquez et al [4] and Y.K. Hong and al [5]. It's designed according to the ATSM D4935 Norm.

2. Manufacturing of composites with nano-fillers resin

In the manufacturing of the material, two phases are followed: dispersion of carbon black fillers in the resin and an infiltration process of the filled resin in the preform.
The used carbon black is Ensaco 250G. It is a porous powder of spherical particles, of average diameter 45 nm assembled in aggregates. The aggregates extension can reach several hundred nanometers and exceed the micrometer (Fig.1).

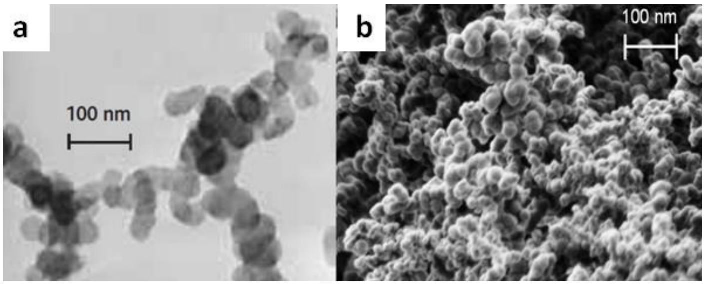

Figure 1. Ensaco 250G Scanning Electron Microscopy

Carbon black is dispersed in a vinylester thermosetting resin (POLYLITE PD-6184), with high performance and low styrene content. Its density is around 1.09 (supplier data). The primary consideration in the selection of this resin is its low viscosity: 85 to 100 mPas at 23°C according to standard 2460-001.
Composite materials are realized with taffeta fibrous glass reinforcements, with a surface weight of 500g/m^2. We choose taffeta because it is well-balanced reinforcements, which allow a homogeneous migration of the resin front in both directions (weft and chains), by liquid way process RTM-Eco or infusion, contrary to unidirectional reinforcements.

2.1. Dispersion of carbon black fillers in the resin

The key challenges in the elaboration of this composites, involve the fillers dispersal in the matrix, and the rheology control of the filled resin. Thereafter, the carbon black rates in studied materials are calculated in volume by report the quantity of the resin and vary from 5 to 25%.
The implementation of the filled resin was carried out by mechanical stirring with a high shear mixer type Silverson L5. The components (polymer and carbon black) are mixed at a speed of 10000 rpm for 20 min. Both parameters have been optimized from the electrical and solution homogeneity. [6]
During the dispersion of the solution, a pronounced non-linear increase in viscosity from 15% carbon black. This is explained by the fact that the powder has a porous and branched structure, but also by the formation of physical interactions between the matrix and the fillers [7]. The increase in viscosity leads also to trapped porosity during polymerization.

Finally, the viscosity is a key parameter for the injection filled-resin into fibrous reinforcements, a using the conventional processes such as infusion and the RTM-Eco (Resin Transfert Molding). An important increase in viscosity can affect the manufacturing by a liquid way of such materials.

2.2. Morphology properties

For the study of the morphology properties and the dispersion state of the carbon black in the matrix, a Scanning Electron Microscopy is used. (Fig.2)

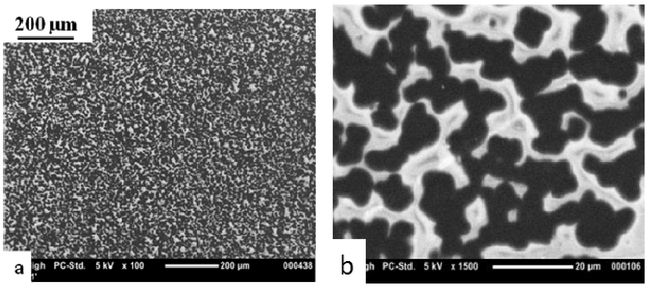

Figure 2. Dispersion state for filled resin with 25% of carbon: a- 200 µm scale, b- 20 µm scale

The dispersion of carbon black powder depends strongly of the size and morphology of constituent particles. However the mixing dispositive with high shear allowed to reduce the granules size and to get a homogenous dispersion.
The micrographs presented in both figures show a uniform dispersion of carbon black fillers in the matrix and the absence of granules. We observe agglomerates connected also called cluster agglomerates. The agglomerate size varies from 5 to 100 microns. Having a structure in the clusters form, favors the creation of conductive path with a low carbon black concentration. [8]
In the case of the thermosetting resin, it is difficult to reduce the agglomerates size to obtain aggregates of a few tens of nanometers. The increase of temperature is an obstacle which limits the duration and speed of mixing, contrary to thermoplastic resins and elastomers.

2.3. Electrical conductivity

The evaluation of the electric behavior of the filled resin is carried out measuring the conductivity on realized samples where a simple and high shear mixings are used. The objective of these experimental tests is to show the dispersion effect on the electric properties of the filled resin. Figure 3 illustrates the evolution of the conductivity in terms carbon black rate.

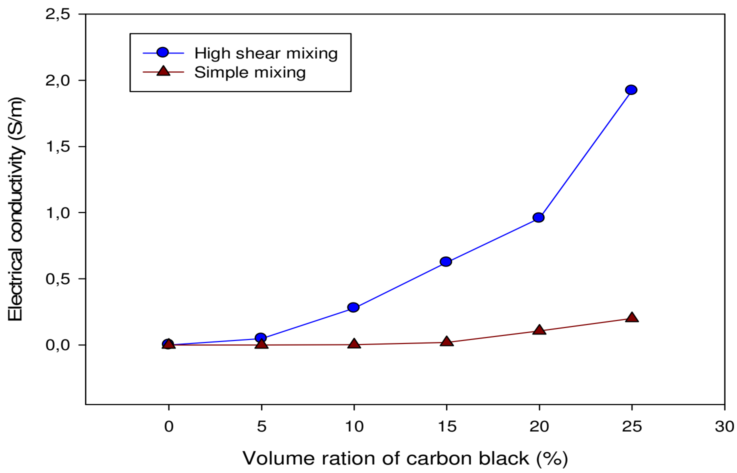

Figure 3. Evolution of the conductivity in terms of the carbon black rate

The use of high shear mixing offers a significant improvement when compared to the simple mixing. Also according to figure 3, the reduction of the granules size of carbon black allowed increasing the conductivity ten times for a volume rate of 25%.
The change from electrical insulation to conductor is done with low concentrations. The percolation threshold is less than 5% of carbon black fillers for the material obtained by high shear mixing. There is between 10% and 15% for material realized with a simple mixing. We can conclude that the formation of a conductive network is obtained at lower rates, by improving the state of the dispersion and morphology of carbon black (tab.1).

Resin + 25% carbon black	Percolation threshold	Electrical conductivity
Simple mixing	10%-15%	0.19 S/m
High shear	<5%	1.9 S/m

Table 1. The filled resin electrical properties of 25% carbon black

2.4. Electrical conductivity

In this study, the injection of the filled resin in the preform is realized using two processes: infusion and RTM-Eco. The choice of the best process corresponds to the process which promotes the migration of the filled resin. However two criteria are imposed for the selection: the state of plate's homogeneity and the electric conductivity. The plates are realized with a filled resin with 25% carbon black.
It seems difficult to obtain a homogeneous distribution of fillers in plate with RTM-Eco. Indeed resin migration is accompanied of an important filtering effect by the fibrous preform. This observation justifies the elimination of this process (Fig.4). [9]

Figure 4. Filtering effect during process

For infusion, we note a progressive migration of the resin into the preform without difficulty, until the complete impregnation of the preform. Visually, after demoulding, we found no filtering effect in the obtained plates. These observations don't exclude the presence of carbon black filtration between the injection point and aspiration, and they don't allow estimating the homogeneity quality of our plates.
In order to evaluate the homogeneity state, we realized an electrical conductivity measurement across the plate, as show in figure 5.

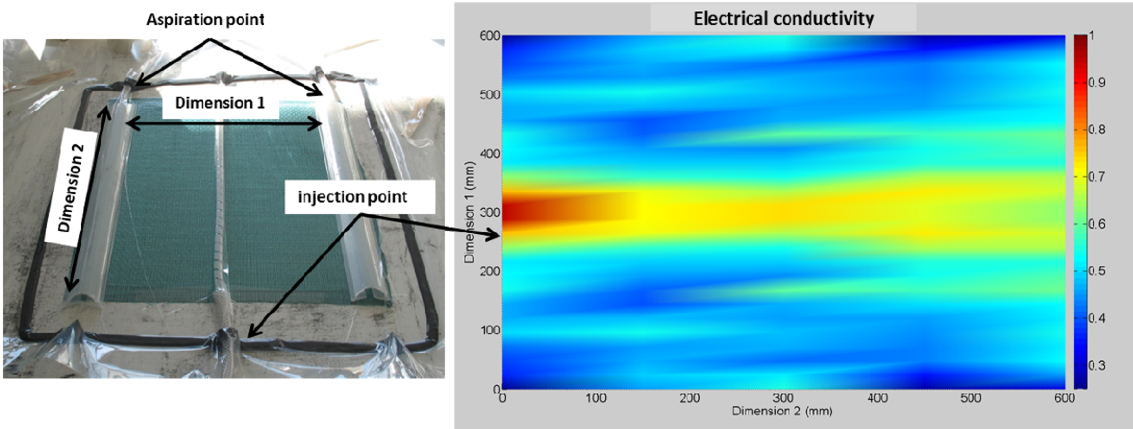

Figure 5. State and cartography of electrical conductivity for infusion

We have a heterogeneous plate with a maximal conductivity at the injection point which is about 0.9 S/m. This conductivity degrades according to the distance traveled by the resin front. (a loss of 70 % between the extreme values). The average value of the electric conductivity is 0.51 S/m with a standard deviation of 0.10 S/m.

For improving the homogeneity and avoid the filtration effect of carbon black by the preform, the solution is to minimize the distance traveled by the resin front into the preform. It is obtained by using two injections points, instead of a single central point. With this modification, it is necessary to add a third aspiration point in order to balance the depression inside the preform (Fig. 6a).

The optimization of the process is validated by the electric conductivity measurements in all plate, as previously. This modification allows improved the homogeneity as the cartography shows it above (Fig. 6b).

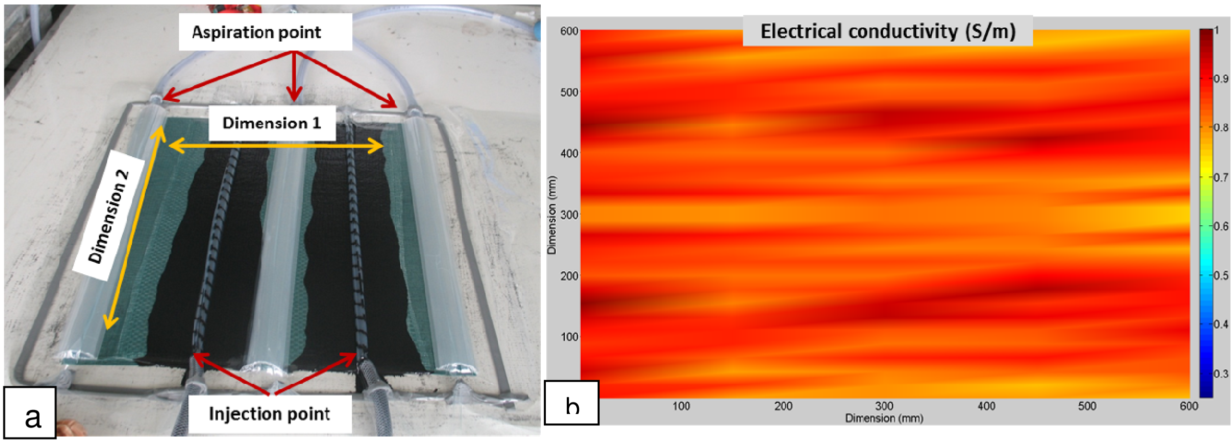

Figure 6. State and cartography for improved solution

We observe a significant improvement of the homogeneity state and the conductivity in the plate, the average conductivity is of the order of 0.85 S/m with a standard deviation of 0.05 S/m. The average conductivity is close to the conductivity of the filled resin in injection point, which shows no filtering effect by the preform. The disparity of the conductivity can result in the uncertainty of measurement device [10].

Finally the obtaining of composite nano-filled resin has required the reduction of the carbon black granules size and improvement of the infusion process minimizing the distance covered by the resin front.

3. Shielding effectiveness of the composite material

3.1. *Measurement device description*

Performances of shielding are obtained using a specific device developed by H. Vasquez et al [4] and Y.K. Hong and al [5]. It's designed according to the ATSM D4935 Norm.
Figure 7 shows a block diagram and photography of the complete device. The measurement is done in transmission normal to the plane of the material which is placed between the source and signal analyzer. The radiated wave on the level of sample is considered as plane, because the distance source-sample is higher than $\lambda/2\pi$ for all range frequency. The frequency band extends from 10MHz to 6GHz.
Both samples per material are necessary to be tested in the order to realize an objective measurement and independent of the thickness. The samples are placed between two successive half-cell connected to a vector network analyzer, which directly measures the transmission (S12, S21) and reflection coefficients (S22, S11) of the waves on each access (or "ports").

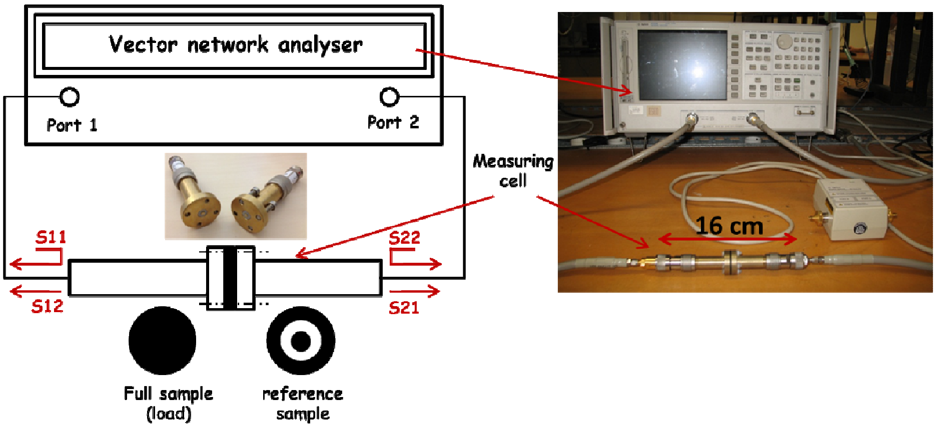

Figure 7. Shielding effectiveness device

The ratio between the transmission coefficients S21 measured with the reference sample holes (ref (1)) and the measurement sample full (load (2)) expressed in decibels gives directly the shielding effectiveness transmission (SE), and it's computed from the rate of the power (P) of the electric field (E) and the power of electromagnetic field or the power of transmitted and incidents waves using the following equation:

$$SE = 10\log\frac{P_1}{P_2} = 20\log\frac{E_1}{E_2} = S21(1)_{dB} - S21(2)_{dB} \quad (1)$$

3.2. *Measurement device description*

The evaluation of the shielding effectiveness was performed on a composite with three glass fibers layers, realized by the injection of resin loaded to 25% of carbon black fillers. During manufacturing, a gel coat was integrated with the same load rate of carbon black fillers, to improve the surface quality of the sample. Figure 8 shows the shielding effectiveness of the laded resin composite with gel coat.
The obtained result shows effectiveness of the order of 6 - 8 dB, corresponding to an attenuation lower than 69 % of the transmitted electromagnetic field. We find attenuation near the loaded resin attenuation (7dB) within glass fibers. Although, the filled resin composite has a largely lower conductivity (0.85 S / m) than the loaded resin (1.9 S / m) at 25%. Is it possible to attribute this improvement to the addition of the gel coat.

This attenuation is low and insufficient to ensure a good shielding, despite the integration of conductive carbon fillers in the composite. It is noted, that the insulating character of the glass fibers is not conducive to the electromagnetic shielding.
A reflection was carried out on improvement of the electromagnetic shielding effectiveness by replacing the glass fibers with carbon fibers. This solution is potentially promising if we improve the composite conductivity by the introduction of filled resin instead of the insulating binder (unfilled resin).

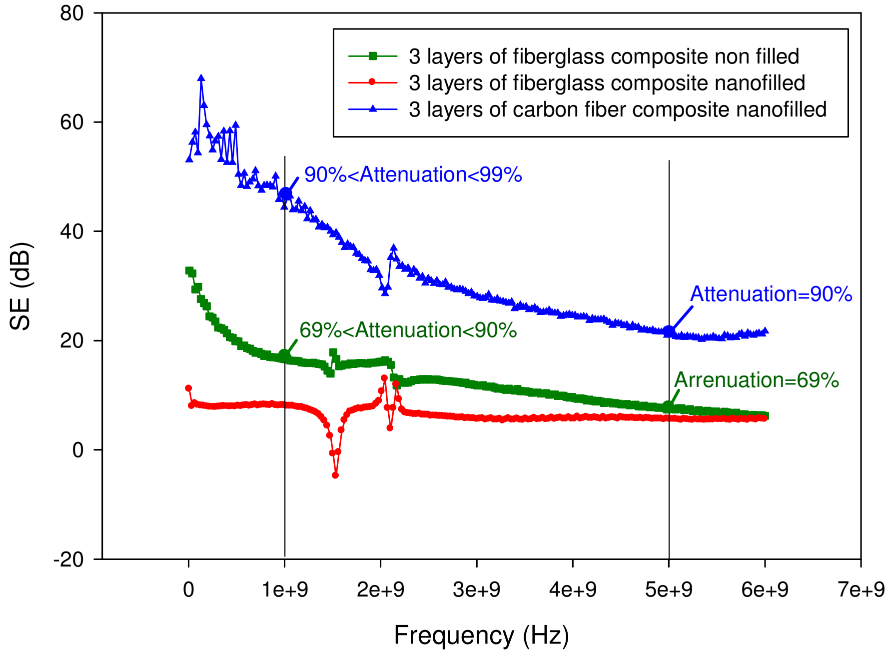

Figure 8. Shielding effectiveness comparison for several composites

Fiber carbone composite without carbon black fillers shows a shielding effectiveness in a range from 8 to 30 dB (Fig. 8). For 1 GHz this effectiveness allows an electromagnetic shielding attenuation between 69 % and 90%. This attenuation decrease with the frequency and at 6GHz we obtain 69% attenuation of the transmitted electromagnetic field.
We note that the unfilled carbon fiber composite provides better shielding effectiveness than filled glass fiber composite.
This assessment led to the fillers addition in the on carbon fiber composite in order to provide a better shielding effectiveness. Results obtain shows significantly higher shielding effectiveness in comparison of unfilled carbon fiber composite. For 1 GHz the shielding effectiveness gain is 36 dB, corresponding to 99% attenuation of the transmitted electromagnetic field. For 6 GHz, the gain is 20 dB, corresponding to 90 % attenuation.
In conclusion, the incorporation of carbon black filler in carbon fiber composite doubles the shielding effectiveness in the 10 MHz-6GHz frequency range. This incorporation increases the shielding effectiveness with a gain value between 50 and 20 dB.

4. Conclusion

This study shows the effect of the size and the carbon black morphology on the electric behavior of the thermosetting resin. Indeed the reduction of the size of carbon black granules in the matrix allows obtaining a weak percolation threshold and a significant improvement of electric conductivity. Also, it promotes the infiltration of the filled resin through the fibrous preform retaining the principle of infusion composite manufacturing. Finally the composite material with carbon black has a good electromagnetic shielding in comparison to the composite material without carbon black. Different applications can then use this new material to improve electromagnetic protection of embedded systems particularly in the domain of transportation.

Many perspectives are possible like:

- A process optimization with a better cooling during the mechanical stirring to reduce the medium fillers size and get aggregate with strong bonds.
- The influence of the carbon black fillers on mechanical behavior of composite which would be investigated with nondestructive acoustic testing during quasi static loading in order to identify damage mechanisms. A next step should be the mechanical fatigue study of these carbon filled carbon fiber composite

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