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Effect of filtration in functionalized and non-functionalized CNTs and surface modification of fibers as an effective alternative approach

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ABSTRACT

Fabrication of multiscale composites by the addition of CNT in epoxy matrices as previous step to the impregnation process leads to several manufacturing difficulties associated to filtration effects and viscosity increments. These effects have been analyzed finding a relation between the type of CNT and the dispersion degree with the change in the rheological behavior and the heterogeneity of the mechanical properties. This heterogeneity is associated to filtration effects of the nanoreinforcement. Modification of the carbon fibers by a nanoreinforced sizing has been presented as an alternative, obtaining homogeneous composites and avoiding the filtration effects. These multiscale composites have higher electrical and interlaminar mechanical properties.

1. Introduction

The use of continuous fiber reinforced polymers (CFRP) increased a lot during the last century and this tendency still remains in the field. They present extremely good mechanical properties while their density is very low [1]. Consequently, the use of these materials is very interesting in those fields in which the structure density must be reduced as much as possible, such as most of the transport devices and wind blades [2].

Although the use of nanoreinforcements has resulted in extraordinary improvements in mechanical, electrical and thermal properties of polymer matrices, (even at very low concentrations) [3,4]; the overall behavior of these nanocomposites cannot reach the mechanical performance of traditional CFRPs. This is mainly due to the volume fraction added and the lower orientation capability when compared to CFRPs. Because of that, structural components with very strict mechanical restrictions, currently manufactured with CFRPs, cannot be replaced by nanocomposites [5].

As an alternative, the addition of nanoreinforcements in traditional CFRPs can result in the modification of their properties leading to new opportunities [6]. This type of materials can be named as multiscale reinforced composites since they combine both micro- and nanometric scale reinforcements. These materials could provide two different behaviors:

- Structural capacity provided by the continuous fiber and even improved by the addition of nanoreinforcements [7].
- Functional capabilities related to the modification of the electrical and thermal properties of the composites, among others.

This combination of functionalities and structural capability would allow them to act as multifunctional materials [8]. Among other possibilities, they are currently being studied to act as intrinsic sensors of the mechanical integrity. The addition of multiwalled carbon nanotubes (CNT) results in electrical conductive networks based on nanoparticles. They are modified when the material is subjected to mechanical loading and, consequently, strained. The measurement of the electrical conductivity variation could be correlated to material strain resulting that the material itself could act as strain sensor [9–12].

Manufacturing of multiscale reinforced composites can be done by several approaches, being the addition of CNT into the resin one of the most commonly studied and used. This approach takes advantage of the methods developed for the manufacturing of nanocomposites based on thermoset resins. The only difference would be the use of this nanoreinforced resin to impregnate the continuous fibers prior to the curing process. There are many research activities regarding the optimization of main

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nanocomposites manufacturing parameters, such as the dispersion methods [13–15].

Nevertheless, the use of these nanoreinforced resins to do the fiber impregnation can present difficulties due to viscosity increments and the possibility of filtration during the impregnation process [16]. Rheological behavior of thermoset resins is modified by the addition of CNT. Gel time and viscosity are very important parameters when using wet routes for composites manufacturing as they have a great influence on the available time and the duration of the infiltration process. On the other hand, the presence of non-completely dispersed nanoreinforcement, which is always found with most of the dispersion strategies, may lead to filtration effects since they could be stopped at small gaps of the fiber fabric (cake filtration). Although this effect can be affected by the size and amount of CNT aggregates, it has been suggested that dispersed CNT or very small aggregates can also cause filtration by their accumulation at small gaps causing their blockage (deep-bed filtration). A schematic view of both phenomena can be observed in Fig. 1.

The addition of CNT onto the fabric, instead of the addition in the thermoset matrix, would avoid the problems mentioned above. Electrophoretic approach [17], catalytic growth [18] of CNT on carbon fiber surfaces and the use of nanoreinforced suspensions to impregnate their surfaces [19], could be used for this purpose. Nevertheless, some of the techniques currently studied present several problems. As an example, the use of chemical vapor deposition of CNT over carbon fibers leads to degradation carbon fibers degradation and, consequently, the strength of the composites manufactured could be reduced [20,21].

CNT incorporation in the carbon fiber sizing could be a good alternative since it could cover the carbon fiber surface generating a homogeneous nanoreinforcement distribution on the fabric surface.

The effect of the addition of different types of CNT (both non-functionalized and amine-functionalized) on the viscosity of an epoxy resin has been studied in order to evaluate difficulties when adding high CNT concentrations. These difficulties are due to viscosity increments above recommended values for infiltration processes, as well as filtration effects. A nanoreinforced sizing has been used as alternative to prove its effect on the electrical and mechanical properties of the traditional CFRPs. In this way, the article proves with clear evidences the filtration effect, the rheological modification and cure kinetics (gel time shift) and it propose an alternative method which is easy to implement as non-functionalized CNT has been used (no need of reaction with the sizing). The aim of testing this method is mainly obtaining composites with improved electrical properties through thickness direction in carbon fiber laminates, while avoiding the problems observed in the first method tested.

When nanoreinforced sizing is used instead of a doped resin, some improvements were observed, both in terms of composite electrical conductivity and mechanical properties which depend on the matrix (interlaminar shear strength and fracture energy).

2. Experimental procedure

2.1. Materials

The materials were manufactured using a two component epoxy resin based on bisphenol A (*Araldite 556* from *Huntsman*) and aromatic amine as hardener (*XB3473* from *Huntsman*). This epoxy resin is a commercial formulation with low viscosity to allow easier impregnation of fiber fabrics by wet manufacturing approaches.

CNTs used were provided by *Nanocyl* as short thin multiwall carbon nanotubes both non-functionalized and amine-functionalized. They are commercialized as *NC3150* and *NC3152*, respectively.

The nanoreinforced sizing was also a commercial formulation from *Nanocyl* with commercial name: *Syzicil XC R2G*. This sizing is compatible with carbon fibers and allows incorporating a thin coating of sizing that counts around 0.5 wt.% of the total carbon fiber.

Finally, the carbon fiber fabric used is a satin 5 harness from *Hexcel* based on AS4C carbon fibers.

2.2. Manufacturing

Nanoreinforced matrices were manufactured by the addition of different concentrations of CNT in the epoxy resin (0.1–0.5 wt.%) in order to evaluate the modification of the rheological properties. The

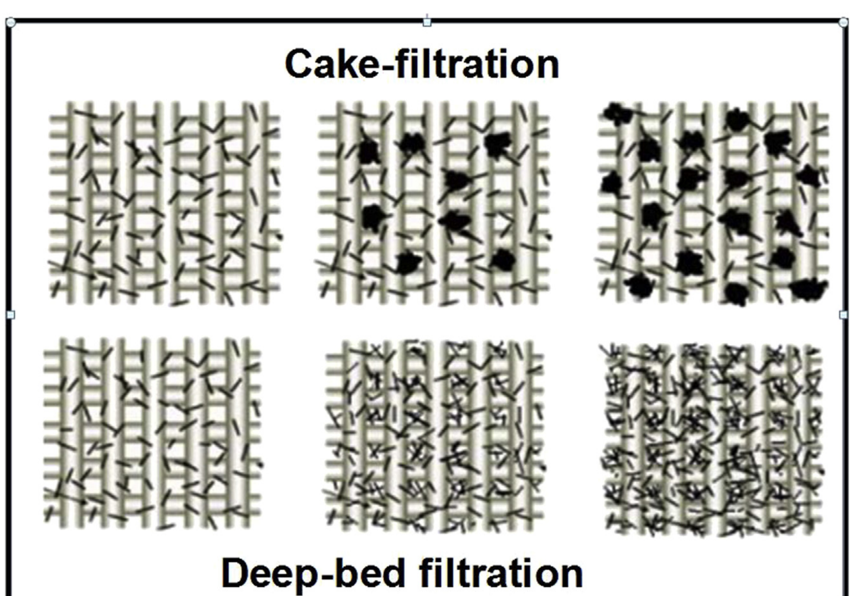

Fig. 1. Schematic view of the different mechanisms of filtration in multiscale reinforced composites manufactured by infiltration techniques.