SURFACE MODIFICATION OF ADVANCE FIBERS TO MANUFACTURE MULTIFUNCTIONAL COMPOSITES

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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 propertie. 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 nanocomposites have better electrical and interlaminar mechanical properties.

1. Introduction

The use of continuous fiber reinforced polymers (CFRP) has increased a lot during the last century and this tendency remains nowadays. 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.

Although the use of nanoreinforcements has resulted in extraordinary improvements in mechanical, electrical and thermal properties of polymer matrices, at very low concentrations [2,3]; 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 cannot be replaced by nanocomposites instead of CFRPs.

As an alternative, the addition of nanoreinforcements in traditional CFRPs can result in the modification of their properties leading to new opportunities [4]. 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 continous fiber and even improved by the addition of nanoreinforcements
- 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 [5]. Among other possibilities they are currently be studied to act as intrinsic sensors of the mechanical integrity. The addition of carbon nanotubes (CNT) results in electrical conductive networks based on nanoparticles which are modified when the material is subjected to mechanical loading and, consequently, the material is strained. The measurement of the electrical conductivity variation could be translated into material strain resulting that the material itself could act as strain sensor [6].

Manufacturing of multiscale reinforced composites can be done by several approaches, being the addition of the CNT in 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 the main parameters related to the manufacturing of the nanocomposites such as the dispersion methods [7].

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. 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 time available 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)

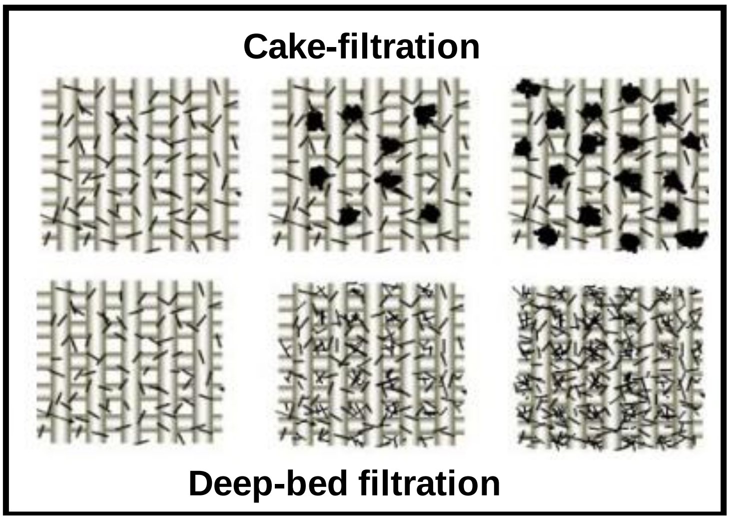

Figure 1. Schematic view of the different mechanisms of filtration in multiscale reinforced composites manufactured by infiltration techniques

The addition of CNT onto the fabric, instead of the addition in the thermoset matrix, would avoid problems mentioned above. Electrophoretic approach, catalytic growth of CNT on carbon fiber surfaces and the use of nanoreinforced sizings 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 onto carbon fibers leads to degradation of the carbon fibers and, consequently, the strength of the composites manufactured could be reduced [8]. The use of current electrophoretic approaches does not lead to good and homogeneous distributions of the nanoreinforcement on the carbon fiber surface.

The addition of CNT in the carbon fiber sizing could be a good alternative since it could cover the carbon fiber surface generating a homogeneous and continuous 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 prove the difficulties when adding high CNT concentrations due to increase in viscosity above the recommended values for infiltration processes. Also, filtration effects have been studied. A nanoreinforced sizing has been used as alternative to prove its effect on the electrical and mechanical properties of the traditional CFRPs. Improvements in terms of electrical conductivity of the composite and mechanical properties which depend on the matrix properties (interlaminar shear strength and fracture energy) were observed when nanoreinforced sizing is used instead of a nanoreinforced resin.

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 amines 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*, reference *Syzicil XC R2G*. This sizing is compatible with carbon fibers and allow incorporation of a thin coating of 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 dispersion of the nanoreinforcement in the epoxy matrix was achieved by means of a three roll mill machine or mini-calendering following a sequential method optimized in previous research works [7].

Panels manufactured by sizing needed two steps prior to the resin infiltration step: i) ultrasonication of the sizing formulation in water to get a more homogenous distribution of the nanoreinforcement, ii) impregnation of fibers with the sizing. The impregnation was done

by means of vacuum assisted procedure using a set-up similar to the one used in the vacuum assisted resin infusion molding process (VARIM). It was carried out at room temperature and dried in stove at 100 ºC during 24 hours.
Afterwards, epoxy matrices (with and without MWCNT) were used to impregnate carbon fiber fabrics (with or without nanoreinforced sizing) by VARIM with a vacuum pressure of 0.6 bar. 30 x 20 cm panels were manufactured following this procedure in which the resin and vacuum inlets were place at the two short sides of the panel. Resin flowed from one short side to the other (longitudinal flow of the resin) until it reaches the opposite side of the panel.

2.3 Characterization

Microscopy techniques were used to evaluate presence of aggregates and well dispersed MWCNT as well as distribution of both elements. For this purpose, two different microscopes were used: Scanning Electron Microscopy (SEM) using *S-3400N* model from *Hitachi* SEM, and a Field Emission Gun Scanning Electron Microscope (FEG-SEM). Surfaces were previously treated with a Pt coating of 6 - 8 nm.

Viscosity was measured using a viscosimeter model *Visco Easy-R* from *Scott* at different temperatures. The differences in viscosity of the mixtures lead to the need of modifying the rotational speed of the screw, from 1 to 200 rpm, depending on the mixture analyzed.

Interlaminar shear strength (ILSS) was tested following the ASTM standard D2344 using a three point bending tool designed for a universal mechanical testing machine from *Zwick.*

Electrical conductivity was measured using a sourcemeter from *Keithley* and measuring the current intensity at different voltages. By applying Ohm's law, resistivity was obtained and, from this value, conductivity was estimated. By changing the surfaces on which the cables were connected, electrical conductivity could be measured through thickness direction or in fiber direction. In order to reduce contact resistance, cables were stuck on the surfaces using silver paint.

3. Results

In order to establish the problems of the addition of CNT in the epoxy resin when it is going to be used as matrix for CFRPs manufactured by wet approaches, viscosity measurements were performed at 60 ºC. This temperature was selected in order to avoid reduction of the gel time due to elevated infusion temperatures.

It was found that contents of non-functionalized MWCNT led to huge increments in the viscosity of the mixtures even at low contents, slightly above 0.2 wt.%. Figure 2 shows a green area that suggests a limit in the viscosity of mixtures that are going to be used in VARIM or RTM processes. Taking this into consideration, it can be establish that contents above 0.2 wt.% of non-functionalized MWCNT require higher infiltration temperatures in order to avoid impregnation problems. Nevertheless, this is not advisable as, the gel time would be reduced with the increase in temperature.

On the other hand, the use of amine-functionalized CNT does not cause the same huge increase in viscosity. This effect was explained by the poorer dispersion of this type of CNT. Although it could be interesting because of the easiness to impregnate fabrics with this type of

CNT, it has to be taken into account that poorer dispersion may lead to *cake filtration* effects, as it was explained in the introduction section (Figure 1).

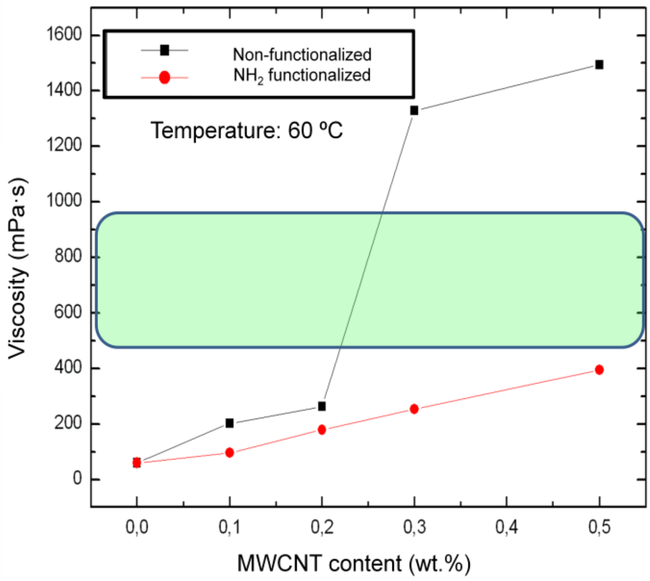

Figure 2. Viscosity evolution with MWCNT content for both types studied.

Variations in the gel time with MWCNT contents must be studied since higher temperatures could be required to carry out the impregnation process due to high viscosity of the mixtures.

It was observed a reduction of the gel time with the addition of non-functionalized CNT even at very low contents (Table 1). This reduction was also found for higher CNT contents (above 0.2 wt.%). Consequently, the increase in temperature in order to reduce the viscosity of the non-functionalized CNT reinforced mixtures is not recommended, since the combination of temperature and non-functionalized CNT contents may lead to premature gelation of the resin which would lead to incomplete impregnation.

CNT content	Neat Resin	0.1	0.2	0.3
Gel Time (min)	35	32	31	25

Table 1. Gel time values obtained for neat resin and nanoreinforced resin with non-functionalized MWCNT at 140 ºC (curing cycle temperature).

Finally, the filtration effect was analyzed. For this purpose, ILSS test were performed using samples from three different areas: zone 1, zone 2 and zone 3. The higher the number designated to the area, the further the area was from the resin inlet. No clear evidence of differences between areas was observed for materials containing functionalized MWCNT (Figure 3). Nevertheless, differences were observed when non-functionalized MWCNT were used with contents above 0.1 wt.%. Both, materials containing 0.2 and 0.3 wt.% non-functionalized MWCNT showed lower values of ILSS at zone 1, that is, near to the resin inlet. This fact was associated to cake filtration effect in which aggregates could remain blocked at the first part of the materials while good dispersed MWCNT could travel further through the fabric porosity. Good dispersion of the nanoreinforcements leads to better reinforcement and increased capability of improving the mechanical properties.

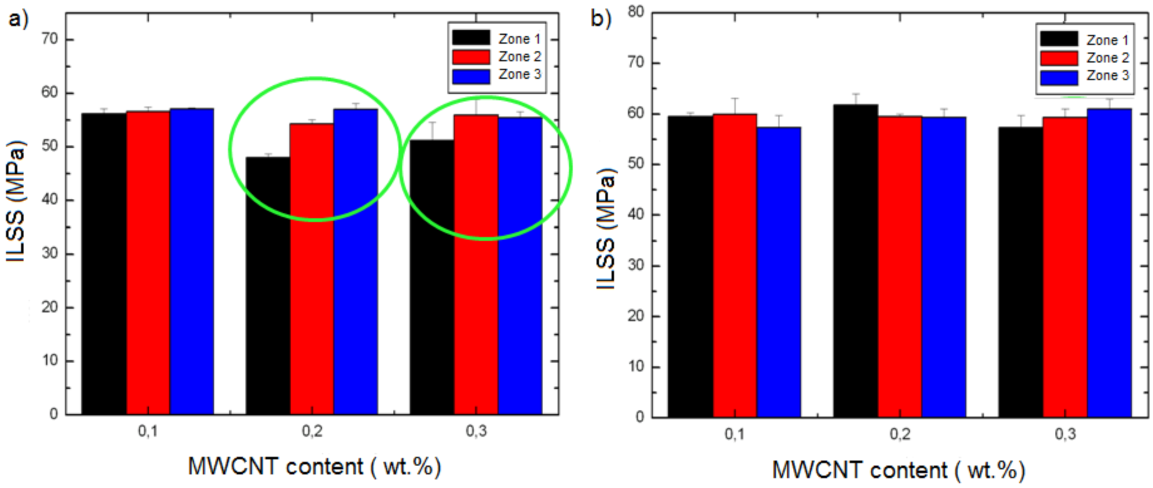

Figure 3. ILSS results at different areas of multiscale reinforced composites containing different contents of both types of MWCNT studied: a) non-functionalized, b) NH_2-functionalized

In order to observe the presence of different amount, morphology or distribution of the nanoreinforcement and its aggregates, different specimens were fractured by separating composite plies through delaminations originated during the ILSS tests (Figure 4). Materials near the resin inlet showed the presence of aggregates which were acting as stress concentrators (Figure 4.a) and, consequently, favouring crack propagation and delamination. Moreover, some areas showed extremely high amount of nanoreinforcement not aggregated (Figure 4.b). These images prove that both, cake and deep-bed filtration, take place during the impregnation of the fabrics with nanoreinforced resins.

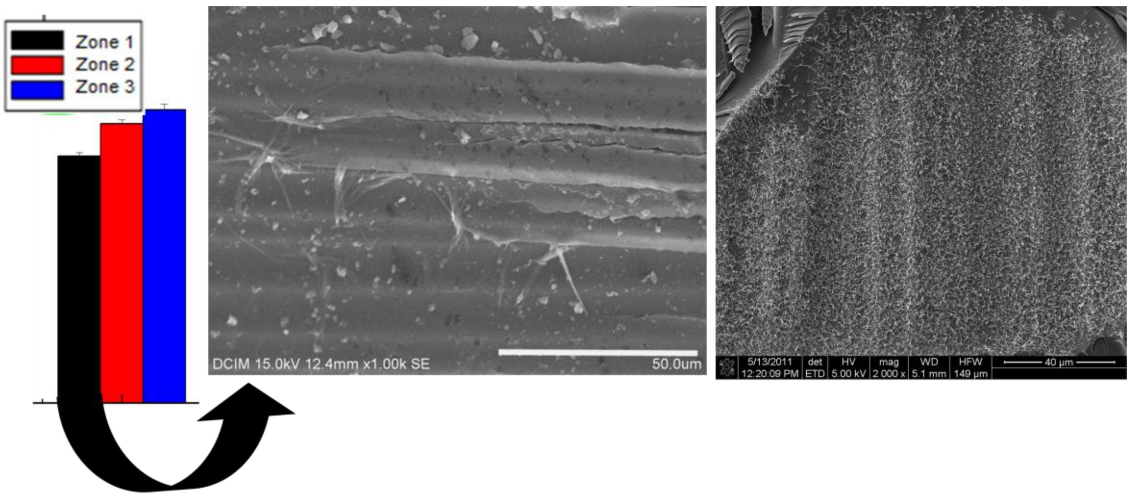

Figure 4. Fracture surface images obtained by SEM and FEG-SEM of tested specimens taken from zone 1 of multiscale composites manufactured with non-functionalized MWCNT.

Observation of fracture surfaces of specimens tested from the Zone 3 showed higher presence of well dispersed MWCNTs (Figure 5). These well dispersed MWCNTs contribute to the increase of the ILSS as they could reinforce better the polymer matrix. This effect could be the reason of the rougher texture observed on these fracture surface images when compared to those observed where higher accumulation of nanoreinforcement or presence of aggregates were found (Figure 4).

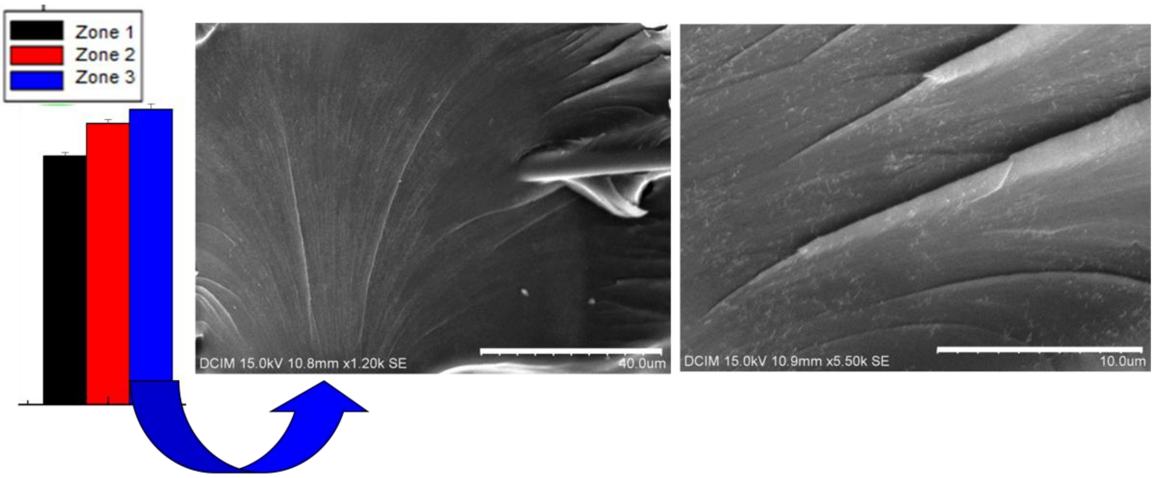

Figure 5. Fracture surface images obtained by SEM and FEG-SEM of tested specimens taken from zone 3 of multiscale composites manufactured with non-functionalized MWCNT.

The use of sizing avoid this effects as the resin rheological properties are not affected by the addition of any nanostructure and the filtration effect is also avoided, thus, obtaining more homogeneous final composites. The preliminary results obtained by the coating of the carbon fibers by means of a MWCNT nanoreinforced sizing showed an increase in the ILSS properties with respect to the addition of MWCNT contents in the resin (Figure 6). The increase of the electrical properties measured through thickness direction (Z direction) is very high when the nanoreinforced sizing is used due to the homogeneous coating with the conductive sizing between the different layers. Consequently, these materials seem to be very promising when thinking about CFRPs with improved electrical properties for electromagnetic shielding or self-sensing capability (Figure 6). On the other hand, the addition of MWCNT in the resin caused a decrease of most of the properties, even the electrical ones, due to poorer impregnation and presence of defects when compared to the reference panel (neat resin with not coated fabric). The change in the rheological properties leads to difficulties during manufacturing process that reduce the effect of the addition of MWCNT and even cause slight decreases of the main properties.

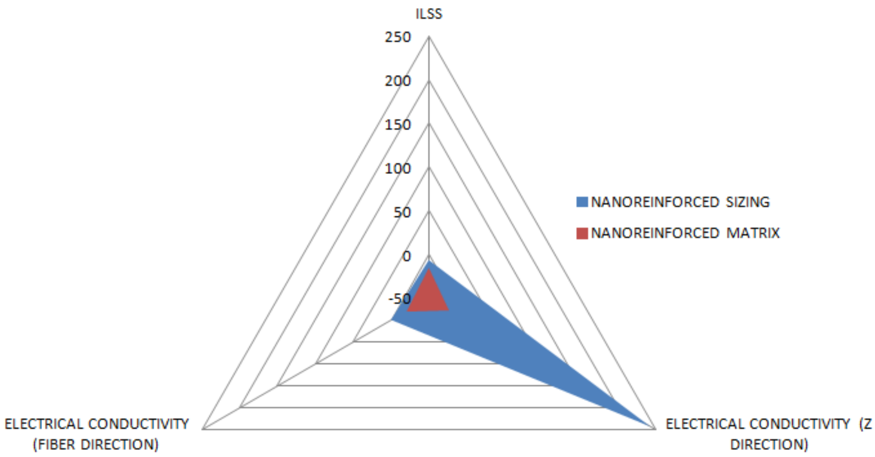

Figure 6. Main variations with respect to the reference material on ILSS, and electrical conductivity, by the addition of MWCNT contents in the epoxy matrix or in the sizing coating of the carbon fibers.

Conclusions

The addition of MWCNT in the epoxy resin to manufacture multiscale reinforced composites caused modification of the rheological properties as well as filtration effects. Both effects lead to non-homogeneuos composites with reduced improvements of the main properties. This effect is more significant when contents above 0.2 wt.% of non-functionalized MWCNT are added. Consequently, the contents that could be added to the resin without causing negative effects would be very limited.

The filtration of non-MWCNT takes place at both scales: cake and deep-bed filtration. They cause variations of properties through different areas of the composites.

The use of a nanoreinforced sizing has been presented as an alternative to highly nanoreinforced matrices (contents above 0.2 wt.%). This alternative reduces the negative effect on ILSS properties and it causes an extremely high increase of the electrical properties measured through thickness direction.

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