ANALYSIS OF THE FILTRATION PHENOMENA DURING RTM MANUFACTURING OF MULTISCALE CARBON FIBER COMPOSITES WITH CNT DOPED EPOXY RESINS

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Abstract

Present contribution analyzes the different filtering mechanisms that occur during resin transfer molding of a CNT doped epoxy resin into a carbon fiber preform. Two filtering mechanisms were indentified, which have been called by other authors as "deep bed filtration" and "cake filtration". For it, the influence of different CNT dispersion methods (toroidal stirring and calandering) on the filtering mechanisms was analyzed. Electrical conductivity (X-Y and Z direction) of the manufactured multiscale composites, measured at different distances from the resin inlet were determined, evaluating the influence of those previous mechanisms on the multifunctional behavior of the composites.

1. Introduction

The incorporation of conductive nanoparticles, such as carbon nanotubes or graphene, into carbon fiber reinforced composites (CFRC) has been proposed as method to obtain new functionalities for these structural materials. The potential increase of mechanical properties, mainly those depended on matrix behavior, jointly the increase of electric conductivity could generate a new group of multifunctional composites with potential capabilities of sensing, electrostatic discharge, electromagnetic shielding, light strike protection, etc. Resin Transfer Molding (RTM) has been proposed as an alternative way to manufacture these kinds of composites. However, processing difficulties related with the increase of viscosity associated to the incorporation and dispersion of CNT into the epoxy resin, jointly the high tendency of the CNT to be filtered during the flow of the doped resin through the carbon fiber preforms, are presented as the main problems to obtain the required properties [1,2]

2. Experimental procedure

2.1. Materials and composite manufacture

To manufacture multiscale carbon fiber epoxy composites, previously an epoxy resin was doped with 0.3 weight % of multiwall carbon nanotubes (CNT). Diglycidyl ether of bisphenol A-based epoxy resin was used and the method selected for manufacturing the nanodoped resins was a mechanical approach, which consists of a two stage procedure:

- *Stage 1*: doped epoxy resins by dispersion of CNT using a high speed stirring system (toroidal stirring) (T).
- *Stage 2:* improve the pre-dispersed doped resin produced after stage 1 by calendering using a 3-roll mill (T+C).

The operational conditions for CNT dispersion have been described in previous studies. Once the epoxy matrix was doped, the multiscale reinforced composites were manufactured by resin transfer molding (RTM), using carbon fiber preforms. The used materials and their properties are listed in the following tables:

Table 1: Main properties of the epoxy resin used in the manufacturing process

Density	**Viscosity at 70 ºC**	**Viscosity at 120 ºC**	**Tensile Strength**	**Tensile Modulus**	**Fracture Toughness**
1.14 g/cm^3	200 mPa · s	50 mPa · s	75 MPa	2.89 GPa	168 J/m^2

Table 2: Main properties of the carbon fiber and the carbon fiber fabric 5H

Tensile Strength	**Tensile Modulus**	**Type of fabric**	**Density**	**Fiber Orientation**	**Mass per area unit**
4385 MPa	231 GPa	Satin 5 Harness	1.78 g/cm^3	50% Weft 50% Warp	280 g/m^2

Table 3: Main properties of the MWCNT

Density	**Carbon Purity**	**Metal Oxides Content**	**Average Length**	**Average Diameter**
1.80 g/cm^3	>95%	<5%	1.5 µm	9.5 nm

Coupons of multiscale composites manufactured by RTM were produced using a low pressure injection equipment provided by *Composite Integration*. The injection equipment is constituted by a pressure pot, a control panel and a switch system that allows the connection of different thermocouples. Also, this system had a temperature regulator that allowed keeping the mixture temperature at 80 ºC. On the other hand, the pot can be also under pressure up to 3 bar which could be regulated to the desired value at each infiltration instant. The mold used allowed variation in the panel thickness keeping the same panel area (200 x 300 mm). The mold surface was covered with a release film to avoid panels getting stuck to it. Once placed the carbon fiber preform (formed by stacking 14 carbon fabric plies), the mold was closed and heated to 180 ºC while the resin was heated to 120 ºC. A vacuum pressure of 400 mmHg was applied to eliminate air entrapped within the mold. Afterwards, the vacuum valve was closed and the resin inlet valve opened in order to start the infiltration process. The injection pressure was increased from 1 to 2.5 bars during the impregnation process in order to ensure constant resin flow. As the injection resin took place from the middle of the panel, the resin flow was radial.

2.2. Characterization techniques

The basic characterization of the manufactured multiscale composites consisted on a microestructural study using optical microscopy to determine the presence of molding defects in the material. Observations were done on polished cross-sections of the composite panels cut at different distances from the resin inlet, to evaluate the influence of this parameter on the infiltration defects. Beside, determination of density (ISO 1183, method A) and average porosity (UNE-EN 2564, method B) were carried out. Densities were measured by immersion in water (Archimedes method) by using a Mettler Toledo balance, with a sensitivity of ±0.001 mg, equipped with a density determination kit by means of the buoyancy technique, was used to evaluate the change of density in cured epoxy resins by the incorporation of nanofillers. These measurements were carried out in 3 specimens cut from the same coupon, at different distances of the resin inlet point to analyzed the effect of the CNT filtration on the composite structure. Measurement of electrical conductivity, both through thickness direction (Z) and along length and width axis (X or Y), were done. Electrical conductivities were also measured at different distances from the resin inlet.

All results obtained for multiscale composites were compared with those measured for composites manufactured following the same fabrication route, but using undoped resin. These materials were identified as "reference composite".

3. Results

Figure 1 shows a scheme of the panel manufactured by RTM showing the different samples analyzed in order to determine the filtration effect as a function of the distance regard to the epoxy resin inlet. The size of all the studied samples is 1 x 1 cm.

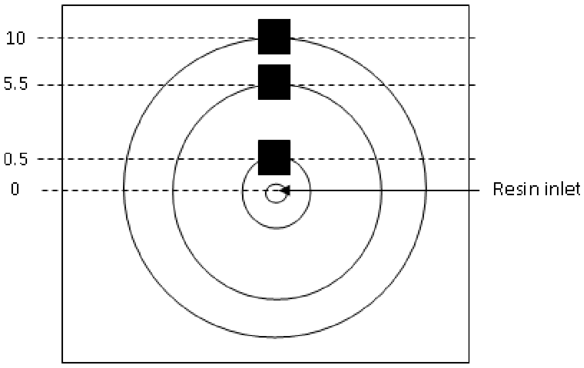

Figure 1. Scheme of the panel manufactured by RTM, indicating the selection of samples for studying the filtration effect. All distances are determined in centimeters, considering the resin inlet as initial point (0 cm).

Table 4 and 5 show the results of the measurements of density, porosity and fiber contents determined for multiscale composites with matrices doped with 0.3 % of CNT. Differences are observed comparing the results obtained when CNT were dispersed by a simple stage of toroidal stirring (T) (table 4) and with a double staged method of toroidal stirring followed by calandering (T+C) (table 5). In the first case, RTM showed as a high reproducibility manufacturing method for the multiscale composites, being able for controlling the rate of reinforcement/matrix along the infiltration length and reducing the proportion of porosity down to 2 % in volume. This conclusion was also confirmed from optical microscopy observations of polished cross-sections of the composite panels (figure 2). However, for better dispersed CNT, that it is the case of using T+C method, lower densities and higher porosities were determined.

Beside, although in both materials, an increase of porosity has been determined when distance form inlet point is longer, this effect is more marked for multiscale composites manufactured with T+C CNT doped resins.

Table 4. Density, porosity and fiber contents of the multiscale composites doped with 0,3 % CNT dispersed toroidal stirring at different distance of the infiltration point.

Properties	Filtering Distance 0.7 cm	Filtering Distance 4 cm	Filtering Distance 10 cm	Average
Density (g/cm^3)	1.4905	1.4680	1.4486	1.4690 ± 0.0209
% Fiber (volume)	56.42	56.50	56.40	56.44 ± 0.05
% Resin (volume)	43.53	41.40	39.81	41.58 ± 1.87
% Porosity	0.05	2.11	3.79	1.98 ± 1.87
% Fiber (weight)	67.38	68.50	69.30	68.39 ± 0.96
% Resin (weight)	32.62	31.50	30.70	31.61 ± 0.96

Table 5. Density, porosity and fiber contents of the multiscale composites doped with 0,3 % CNT dispersed with a combination of toroidal stirring and calandering at different distance of the infiltration point.

Properties	Filtering Distance 0.7 cm	Filtering Distance 4 cm	Filtering Distance 10 cm	Average
Density (g/cm^3)	1.4746	1.4635	1.4555	1.4645 ± 0.0096
% Fiber (volume)	59.54	59.21	60.13	59.63 ± 0.47
% Resin (volume)	37.13	36.67	34.48	36.09 ± 1.42
% Porosity	3.33	4.12	5.39	4.28 ± 1.04
% Fiber (weight)	71.87	72.02	73.54	72.48 ± 0.92
% Resin (weight)	28.13	27.99	26.46	27.52 ± 0.92

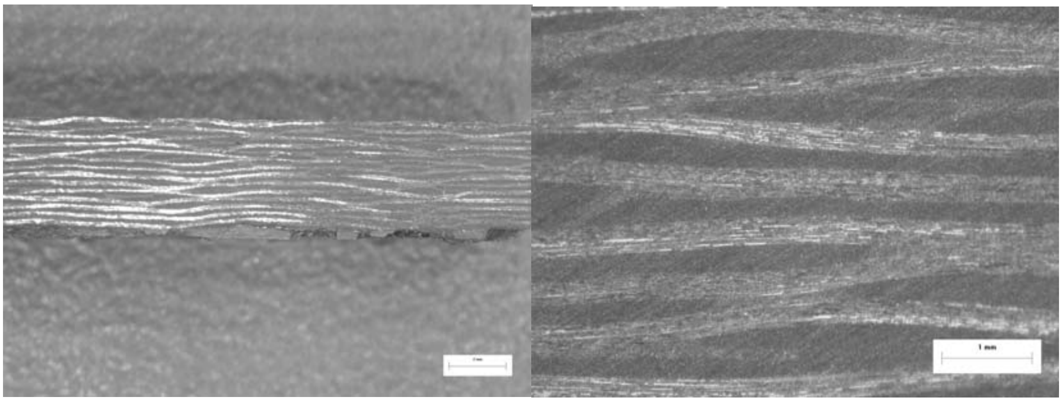

Figure 2. Carbon fiber multiscale composite with 0.3 wt.% CNT doped resin manufactured by RTM.

Table 6 shows the electrical conductivities measured both in reference composites manufactured with undoped resins and multiscale composited made with the same manufacture method but using resin doped with 0.3 wt.% of CNT (NC3100). Obtained results are not enough conclusive, although increases, mainly when the conductivity is measured in Z direction, was determined. Conductivity in XY direction is specially influenced by the carbon fiber, being the values determined for undoped and multiscale composite as quite similar, in the range of 12000-14000 S/m. The values of electrical conductivity along Z show that there is not a fall of the conductivity far from the resin inlet. This implies that the filtration effect is very low. In fact, it seems that a slight increase of electrical conductivity at the end of multiscale panel.

Table 6. Electrical conductivities measured in XY and Z direction for reference and multiscale composites.

Material	Direction	Sample 1 (S/m)	Sample 2 (S/m)	Sample 3 (S/m)	Average (S/m)
Reference	XY	13676	14353	14277	14102 ± 371
	Z	1.45	1.79	1.61	1.5 ± 0.11
0.3 % NC3100 (T)	XY	15243	13670	16715	15209 ± 1523
	Z	2.9	2.8	2.9	2.9 ± 0.08
0.3 % NC3100 (T+C)	XY	12934	12178	12178	13377 ± 1472
	Z	6.8	6.4	5.7	6.3 ± 0.52

4. Analysis of the filtration effect

The filtration of the nanofillers by the fibrous medium may also lead to inadequate final component quality due to an inhomogeneous microstructure. The filtering is caused by the nanofillers being trapped in the inter-tow regions within the fiber perform mesh during fabrication. Filtering is more evident when using nanofillers that have high aspect ratios, such as carbon nanofibers and nanotubes. Two filtering mechanisms can take place during liquid molding of composites with doped resins [1,2]:

- *Cake filtration* takes place when the particles size is larger than the available pore size. This results in the deposition of nanofillers, the “filter cake”, which can build-up ahead of the fibrous medium as soon as suspension enters the mould. This situation is commonly cited as “microscopic” cake filtration. This mechanism can occur especially during tow impregnation and it usually occurs when the CNT/epoxy dispersion present aggregates are larger than the inter-two pore dimension (fig. 3a).

- *Deep bed filtration* is the alternative filtering mechanism to microscopic cake filtration and occurs along the reinforcement length, due to its dual scale nature of intra- and inters- tow channels. This mechanism is characterized by the capture of particles dimensionally smaller than the pore channels. Continuous capture of particles through deep bed filtration can result in the reduction of the available channels dimensions leading ultimately to cake filtration at a microscopic level (fig. 3b).

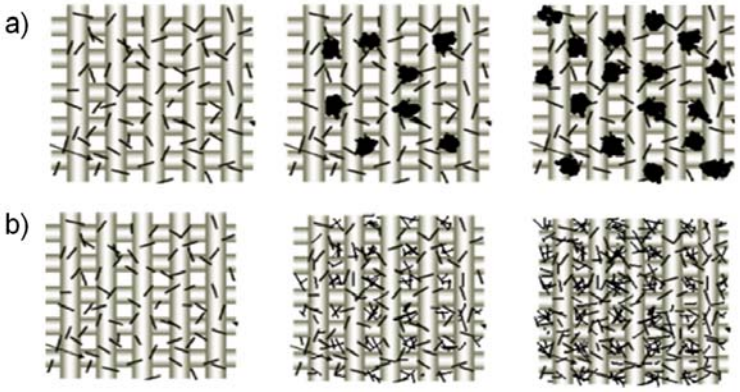

Figure 3. Schematic views of the filtering mechanisms in multiscale composites manufactured by infusion techniques: a) cake filtration y b) deep bed filtration.

Both mechanisms cause clogging of the fibrous porous media, slowing down the resin flow front progression, resulting in longer infusion cycles and filler concentration gradients.

The results showed previously confirm the increase in porosity when resin is nanoreinforced with CNT, being almost inexistent when neat resin is used. This effect was expected because the carbon nanotubes filtering causes microporosity as it was illustrated in figure 3. Moreover, porosity increased as the distance to the injection point did, which agrees with the previous explanation. It was less predictable that porosity also increased when dispersion reached was better, as it was observed for materials based on nanoreinforced resin dispersed by combination of toroidal agitation plus calendering. It can be concluded that these composites presented more accused filtering effect. This effect could be caused by a deep bed filtration mechanism due to the capture of individual and well dispersed CNT by the carbon tows, reducing the resin flow inside them. Although toroidal stirred resins have larger CNT aggregates susceptible to be captured by the CNT fabric pores, favoring the cake filtration at short distances from the resin inlet point, once these aggregates are retired from the resin, the flow of the microscopic filtered resin is more favored.

Respect to the variation of electrical conductivity in Z, for composite materials manufactured with doped resin, it is observed that the highest conductivity measurement was obtained for the material doped with 0.3 wt. % of carbon nanotubes dispersed by combining techniques, toroidal stirring followed by calendering. It means that, although filtering effect is favored when well dispersed CNT are infused into the carbon fabric preform, improving dispersion also favor the formation of a more effective electrical percolation network.

5. Conclusions

Multiscale carbon fiber composited manufactured by RTM using CNT nanodoped resins showed both cake filtration and deep bed filtration mechanisms which generate increase of porosity. Although the application of a less effective dispersion method, such as toroidal stirring, could be reduce the apparent porosity because is favored the microscopic filtration of larger CNT agglomerates at short distance from the resin inlet, it reduces the amount of dispersed CNT available for the generation of an effective electric percolation network. Higher conductivities were measured in the case of doping with well-dispersed CNT, but porosity problems could appeared reducing mechanical behavior of manufactured multiscale composites.

References

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