

ASSESSING THE DISPERSION OF NANOCINCLUSIONS IN NANOREINFORCED CFRP LAMINATES USING ELECTRICAL RESISTANCE MEASUREMENTS

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Abstract

In this work electrical resistance measurements were utilized as a mean to assess the dispersion of Graphene Oxide nanoinclusions into CFRP laminates. This approach involves resistance measurements in the through-thickness and transverse directions of the laminates. Measurements were conducted in CFRP laminates containing Graphene Oxide dispersed into the epoxy matrix with filler contents of 1wt% and 5wt%. The morphology of the samples was examined by means of optical microscopy and scanning electron microscopy. The obtained results suggest that at low filler contents, 1wt%, the dispersion is uniform into the bulk of the sample, while at higher filler loadings, 5wt%, there are indications of non-uniformity due to the formation of areas with higher filler concentration.

1. Introduction

Carbon Fiber Reinforced Polymer (CFRP) composites are being increasingly used in load carrying applications where low weight is required. Despite their excellent mechanical properties, their electrical and thermal anisotropy can introduce challenging problems when CFRPs are exposed to lightning and thermal loads [1-3]. Specifically, the lower electrical and thermal conductivities in the through-thickness and transverse directions, compared to the properties along the fibre direction, pose problems.

The mitigation of the effects of this anisotropic behaviour upon the electric and thermal responses has been focus of scientific research over recent years, and several approaches have been proposed as possible solutions to address this matter [4]. Altering the electrical and thermal properties of the polymer matrix of CFRP laminates has been proven to be an effective method since it can affect the bulk properties of the laminate significantly. This is achieved by the addition of a conducting filler into the resin prior to the manufacturing of the laminate. Considering that resin rich layers exist between the individual laminae, thus hindering heat dissipation and current flow, improving the properties of the polymer matrix will affect the interlaminar region polymer thus enhancing the transverse properties of the laminate. Several conducting fillers have been used in the past; including carbon-

based fillers, e.g. Graphene Nano platelets (GNPs), Carbon nanotubes (CNTs), Carbon black (CB) and Carbon Nanofibres (CNFs), as well as metallic inclusions, like e.g. Silver nanoparticles (SNPs), Silver nanowires (SNWs)[5-8].

From a composites manufacturing point of view, improving the properties of polymer resin systems, in this case epoxies, depends on the successful dispersion of the reinforcing phase into the matrix. For the case of nanoreinforced CFRP the process is somewhat more complex. The majority of the work conducted in CFRP reinforced with some type of a conducting filler dispersed into the resin has involved hand lay-up processes or alterations of prepreg for the manufacturing of the samples [2, 5, 6]. Only recently infusion processes have been reported but not concerning bulk infusion of a laminate with a modified matrix. A major concern in these processes is whether the nanofiller will be homogeneously distributed into the laminate's bulk or it will be "filtered" by the fibres close to the resin inlet.

Graphene Oxide (GO) is a 2D material with a similar structure to Graphene. It is produced by the oxidation of graphite, hence the produced sheets are covered with oxygen. In addition functional groups such as hydroxyl and epoxides are grafted on the basal plane. Finally, carbonyl and carboxyl groups can be found grafted on the edges of the graphene sheets. These groups are responsible for a highly hydrophilic behaviour that makes graphene oxide highly dispersible in water [9]. This behaviour makes GO easily dispersible to epoxies [10].

In this work, as-received GO was dispersed into an epoxy resin system prior to the infusion process. To assess the quality of the infusion and the dispersion/distribution of the nanoinclusions into the laminate's bulk electrical resistance measurements were conducted in the through-thickness and transverse directions.

2. Experimental methodology

2.1. Materials

A two-component epoxy system was utilised, kindly supplied by BASF. The system was consisting of the BaxxoresTM 5300 epoxy resin and the BaxxodurTM EC 5310 curing agent. The components were mixed by weight at a ratio of 100/20 according to the specifications of the manufacturer. The Graphene Oxide (GO) (edge-oxidized) was kindly provided by Garmor Inc, USA, consisting of approximately 10 graphene layers and a nominal particle size diameter of 500nm. Finally, a unidirectional non-crimp carbon fabric utilising Zoltek Panex 35 50K carbon fibres and an areal weight of 882 g/m² was used as reinforcement.

2.2 Manufacturing of nanoreinforced CFRP laminates

The manufacturing process of the nanoreinforced CFRP can be divided into two different stages. The first one includes the dispersion of GO into the epoxy resin and the second the actual infusion process of the laminates. The dispersion of GO into the epoxy was achieved by means of high speed mixing, SpeedmixerTM DAC 150.1 FV. This apparatus operates in way of a dual asymmetric centrifuge that leads to introduction of high shear forces in the mixture, reducing the formation of agglomerates and contributing to homogenous mixtures. GO/epoxy nanocomposite mixtures were prepared in filler contents of 1wt% and 5wt%. GO nanoparticles were added to the epoxy in the specified quantities followed by high speed mixing for 10 min at ambient temperature. After the mixing the curing agent was added and the mixture was hand stirred for 5 min followed by degassing in a vacuum oven at ambient temperature for 10 min. The preparation of the GO/modified CFRP was achieved by means of Vacuum Assisted Resin Transfer Molding (VARTM). Five layers of dry carbon fabric were stacked in a steel plate. To obtain identical surface finish to both sides of the laminate, flow media were placed on both sides of the fabric stack, mold and upper side. After the infusion process the laminates were cured for 6h at 70°C. No noticeable influence on the viscosity was observed after the mixing and during the infusion. The fibre volume fraction of the manufactured laminates was approximately 57%.

Table 1. Composition of the manufactured GO/CFRP samples

Sample/wt%	V_f (%)	V_{GO} (%)	V_m (%)
Neat	57	0	43
1wt%	57	0.015	42.985
5wt%	57	0.075	42.925

2.3 Experimental methods

2.3.1 Electrical contact preparation

Prior to the measurements the samples surfaces that were intended to act as electrodes were initially polished with Silicon Carbide sandpaper, 600 and 1000 grit, to remove the excess polymer from the surface and expose the fibres to achieve direct electrical contact. To mitigate the influence of surface roughness and to promote ohmic contact across the electrode area, an epoxy based adhesive containing silver particles, supplied by RS Components, with a volume conductivity of 10^3 S/cm was employed. A thin layer of the adhesive was applied to the intended electrode surface followed by curing at ambient temperature for 24h.

2.3.2 Electrical resistance measurements- Assessing the dispersion

The DC electrical resistance in the through-thickness and transverse directions of the CFRP samples was measured by means of a two-probe setup with the use of TTi BS-407 milli/micro-ohmmeter. For the measurements in the through-thickness direction disk shaped, 50mm in diameter, electrodes were utilized, a guard-ring was featured in the voltage sensing electrode. For measurements in the transverse direction a PTFE test cell was manufactured. The test cell featured a screw actuator to control the amount of applied pressure, 5 MPa, in the electrical contact area to provide consistency over the measurements. The electric current was injected via copper foils, with a thickness of $35\mu\text{m}$, which were bonded to the test fixture. All the measurements were conducted at a temperature of 25°C and 55% RH. To assess the dispersion electrical resistance measurements were done in the through-thickness and transverse directions in samples that were cut from the manufactured plate as shown in Figure 1. It is known that electric current conduction in the through-thickness direction is affected by the polymer located in the interlaminar region, resin-rich layers between the laminae act as insulating barriers. Thus, resistance measurements in the through-thickness direction are more sensitive to detect the influence of the addition of a conductive inclusion. Assuming homogenous distribution of the filler along the bulk of the laminate, including the interlaminar region, the resistance should exhibit similar values both in the resin inlet side and the vacuum outlet. Deviations between measurements in these locations can be attributed to non-uniform particle distribution, possible creation of areas with higher filler concentration due to filtration of the inclusions from the fibres.

Initially the transverse resistance of the manufactured plate was measured before it was cut in half with the use of water cooled diamond disk saw. In this way two samples for transverse measurements were formed, samples TR-1 and TR-2, to detect possible variations of the dispersion along the resin flow. After this step the samples TT-1 and TT-2 were waterjet cut from the CFRP and measurements were conducted. To provide corrections for parameters such as sample dimensions, the results will be presented in terms of apparent electrical conductivity.

2.3.3 Morphological characterization

The morphology of the manufactured samples was examined by means of optical microscopy, Olympus BX51, and Scanning Electron Microscopy (SEM), Carl Zeiss EVO 50.

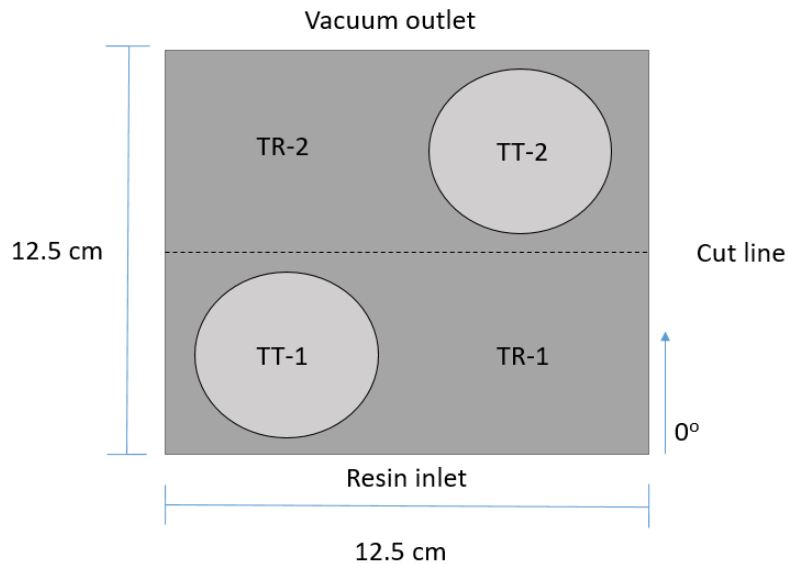


Figure 1. Schematic of the position the samples were cut off, measurement areas (TR: transverse, TT: through-thickness).

3. Results

3.1 Sample morphology

From both the optical microscopy and SEM images the existence of GO inclusions was evident, see Figure 2. While it was possible to detect the GO inclusions with the use of an optical microscope, SEM images were to determine their morphology. From the SEM image below, Figure 2 (right), it can be observed that the shape of the inclusions appears to be flake-like and penny shaped, with the diameter significantly larger than the thickness. The observed dimensions seem to be in good agreement with the ones stated from the supplier of the filler.

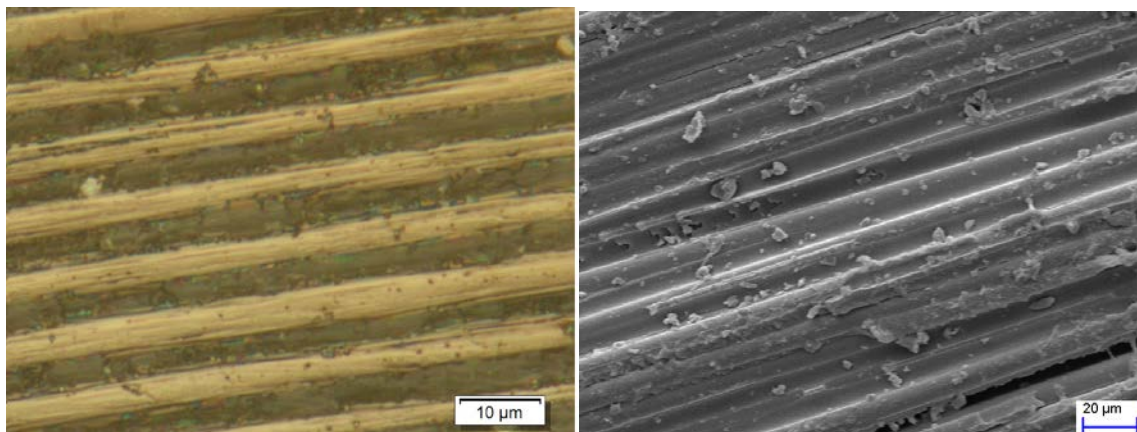


Figure 2. Optical microscopy micrograph (left) and SEM image (right) from the sample 5wt% GO into the epoxy matrix.

3.2 Electrical characterization

Table 2 depicts the results obtained from the characterization of the transverse direction electrical conductivity. It is seen that the addition of GO does not affect the conduction mechanism in this direction. By comparing the results for the individual samples small variations can be observed. In the

case of the sample containing 5wt% GO, the conductivity appears to be slightly increased compared to the rest of the examined systems. This can be associated with the formation of conducting paths between the carbon fibres, as it can be seen in SEM images, Figure 2. By comparing the values for the entire sample with the ones obtained from the two smaller parts of the sample, no significant difference can be identified. This is expected due to the fact that the transverse electrical conductivity is governed by the fibre to fibre contact points and considering that the fibre volume fraction is well above percolation.

Table 2. Transverse direction results

Sample/wt%	<i>Entire sample</i> (S/cm)	<i>TR-1</i> (S/cm)	<i>TR-2</i> (S/cm)
Neat	5.6×10^{-1}	5.68×10^{-1}	5.62×10^{-1}
1wt%	5.48×10^{-1}	5.53×10^{-1}	5.5×10^{-1}
5wt%	5.78×10^{-1}	5.94×10^{-1}	5.82×10^{-1}

The results from the characterization of the through-thickness direction are listed in Table 3. The influence of GO particles appears to be more significant in this direction, i.e. increased conductivity values are observed with higher weight fractions of GO. For the neat system the values exhibit almost identical values, with only a slight variation. The sample containing 1wt% GO exhibits a similar behaviour with a minor discrepancy, with a slightly higher conductivity value close to the resin inlet side compared to the vacuum side. The addition of higher filler content, 5wt%, provides further increase in the through-thickness electrical conductivity. Similarly to the sample containing 1wt% a variation can be observed for the 5wt% GO sample. Although the variation cannot be considered high, it is assumed that close to the resin inlet side the concentration of GO particles is higher than on the vacuum side.

Table 3. Through-thickness direction results

Sample/wt%	<i>TT-1</i> (S/cm)	<i>TT-2</i> (S/cm)
Neat	5.43×10^{-2}	5.51×10^{-2}
1wt%	6.08×10^{-2}	5.90×10^{-2}
5wt%	7.86×10^{-2}	7.08×10^{-2}

Conclusions

A new method to assess the dispersion of conducting nanoinclusions has been presented. By conducting electrical resistance measurements in the through-thickness and transverse directions of the nanoreinforced laminate information about the distribution of the filler can be extracted. The results in the through-thickness direction provided a clearer insight since the conduction mechanism in this direction is affected by the resin rich layers in the interlaminar regions. However, the characterization of the transverse direction did not provide substantial information about the dispersion since fibre contact point dominate the conduction process. While the distribution appeared to be homogenous for low filler contents, some aggregation for higher filler contents leads to non-uniform particle distribution, Figure 3. The technique described although simple has been proven to be effective for probing particle distributions, and shows potential for quality control of nanoreinforced laminates.

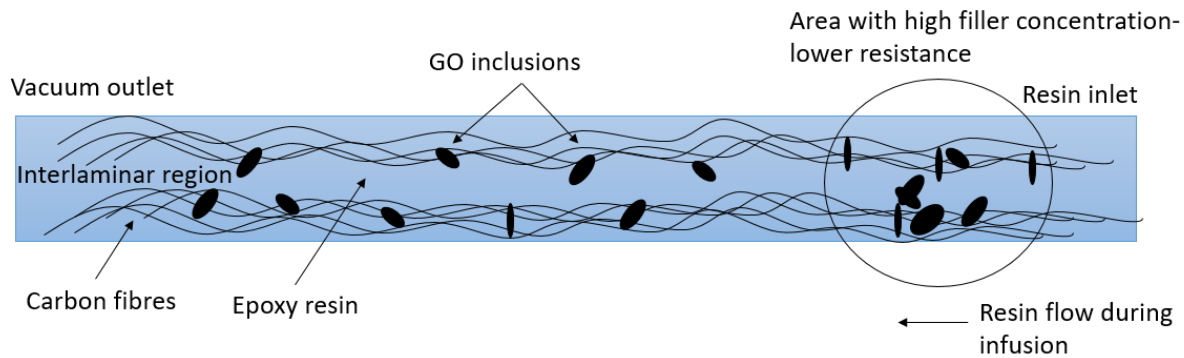


Figure 3. Non-uniform inclusion dispersion

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References

- [1] F. Rachidi *et al.*, "A review of current issues in lightning protection of new-generation wind-turbine blades," *IEEE Transactions on Industrial Electronics*, vol. 55, no. 6, pp. 2489-2496, 2008.
- [2] C. Kostagiannakopoulou, E. Fiamegkou, G. Sotiriadis, and V. Kostopoulos, "Thermal Conductivity of Carbon Nanoreinforced Epoxy Composites," *Journal of Nanomaterials*, vol. 2016, pp. 1-12, 2016.
- [3] P.-C. Ma and Y. Zhang, "Perspectives of carbon nanotubes/polymer nanocomposites for wind blade materials," *Renewable and Sustainable Energy Reviews*, vol. 30, pp. 651-660, 2014.
- [4] W. Qin, F. Vautard, L. T. Drzal, and J. Yu, "Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber-matrix interphase," *Composites Part B: Engineering*, vol. 69, pp. 335-341, 2015.
- [5] I. El Sawi, P. A. Olivier, P. Demont, and H. Bougherara, "Processing and electrical characterization of a unidirectional CFRP composite filled with double walled carbon nanotubes," *Composites Science and Technology*, vol. 73, pp. 19-26, 2012.
- [6] E. Kandare *et al.*, "Improving the through-thickness thermal and electrical conductivity of carbon fibre/epoxy laminates by exploiting synergy between graphene and silver nano-inclusions," *Composites Part A: Applied Science and Manufacturing*, vol. 69, pp. 72-82, 2015.
- [7] S. Han, J. T. Lin, Y. Yamada, and D. Chung, "Enhancing the thermal conductivity and compressive modulus of carbon fiber polymer-matrix composites in the through-thickness direction by nanostructuring the interlaminar interface with carbon black," *Carbon*, vol. 46, no. 7, pp. 1060-1071, 2008.
- [8] I. Gaztelumendi, M. Chapartegui, R. Seddon, S. Flórez, F. Pons, and J. Cinquin, "Enhancement of electrical conductivity of composite structures by integration of carbon nanotubes via bulk resin and/or buckypaper films," *Composites Part B: Engineering*, vol. 122, pp. 31-40, 2017.
- [9] S. Stankovich *et al.*, "Graphene-based composite materials," *nature*, vol. 442, no. 7100, p. 282, 2006.
- [10] R. Atif, I. Shyha, and F. Inam, "Mechanical, thermal, and electrical properties of graphene-epoxy nanocomposites—A review," *Polymers*, vol. 8, no. 8, p. 281, 2016.

