Graphene Oxide - Epoxy Resin Nanocomposites: A Potential Candidate for Improving Lightning Protection Systems of Wind Turbine CFRP Sparcaps

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Keywords: Graphene oxide**,** Nanocomposite epoxy, WT Lightning Protection.

Abstract

Wind energy is one of the fastest-growing sources of electricity worldwide. The emergence of upscaling on the WT size results in research and development on new materials, especially for the WT blades, that will also fulfil the LP requirements. In the present work, graphene oxide (GO) will be utilised as a nanofiller for epoxy resin systems used as binding polymers or adhesives for CFRP components. The main objective of this study is to increase the conductivity of the epoxy resin system without compromising the mechanical and thermal properties. For this purpose, different filler loads of GO were incorporated in epoxy resin matrix in order to achieve increased electrical conductivity. It was found that at 2 % wt filler content of GO the sample exhibits higher conductivity, strongly dependent on the applied electric field. Transmission Electron Microscopy (TEM) was used to examine the structure of the nanocomposite system as well as the dispersion level achieved. The Differential Scanning Calorimentry (DSC) showed no apparent alterations of the T_g of the attained nanocomposite samples. The Young's modulus and tensile strength of the examined samples showed a variation with the filler content without being decreased. The viscometric analysis showed a slight increase of the viscosity as the filler content increases.

Introduction

Carbon fibre reinforced polymer (CFRP) materials are increasingly used for reinforcing large Wind Turbine (WT) blades, due to the high strength to weight ratio they exhibit, and are expected to be utilized even more as the dimensions of the blades grows [1,2]. Although their mechanical properties are superior, the electrical properties need to be considered carefully during the design of the lightning protection coordination.

The main challenge emerging from the presence of uni-directional CFRP components inside WT blades is the electrical conductivity they exhibit which is relatively high compared to the conductivity of glass fibres, but relatively low compared to typical metal conductivities. All wind turbine blades must meet international standard requirements in terms of lightning protection, namely IEC 61400-24:2010 [3]. According to the standard, in the case of additional conductive components being present within the blade, these parts should be designed to conduct their share of lightning current and thus be connected to the lightning protection system [3]. Though, the strong anisotropy of the electrical conductivity to the fibre orientation, especially for uni-directional (UD) CFRPs, requires detailed design considerations for entry and exit points for the lightning current as well as direct attachment to CFRP structural parts. More specifically, the conductivity on the lengthwise direction, of such components, can be four orders of magnitude higher than the conductivities in transverse and through-thickness directions [4, 5]. The high current densities generated during lightning strike incidents can be critical for the CFRP material. The abruptly elevated temperatures, due to resistive heating, might lead to delamination or incineration of the CFRP components [4].

Consequently, reducing or eliminating the anisotropic characteristics of the CFRP material could result in a rapid and uniform distribution of the current throughout the cross-section of the structure and mitigation of the thermal damage. It has been previously demonstrated that coatings with increased conductivity can facilitate the current distribution in the case of direct lightning strikes and prevent damage and delamination phenomena in CFRPs [6]. Carbon-based nanoinclusions are currently being examined as an additive to enhance mechanical, through improved bonding [7, 8] or electrical/thermal properties [9, 10] of FRPs. For the purposes of this study, it is assumed that the infusion of a binding polymer with enhanced electrical conductivity in carbon fibres, will be beneficial by preventing thermal damage associated with resistive heating phenomena.

The aim of this work is to study the incorporation of graphene oxide (GO) conducting nanoparticles in epoxy resin systems used as binding polymers in CFRP materials. Recently, GO has been investigated as a filler to enhance the mechanical properties of polymers [11]. Furthermore, the platelet-like geometry of this material, can result in increased electrical conductivity in lower filler contents, as compared to, traditionally used, often spherical, conductive fillers [12]. Thus, the viscosity (as well as the cost) can be kept at low enough levels, ensuring a likelihood of cost-effective industrialisation of the filler. The incorporation of conducting nanoscale inclusions, such as GO nanoparticles, inside the binding polymer matrix can potentially lead to the formation of a conducting path between the carbon fibres or the carbon fibre layers, which will reduce the composite's anisotropic

characteristics. The material characterization study will be conducted in terms of electrical, thermal and mechanical response, as well as viscometric analysis of the epoxy-based nanocomposite.
The work will be evaluated with reference to the application in large scale blade manufacturing, to foresee the impact on LPS efficiency in future wind turbine blade designs utilizing CFRP.

Methodology

Materials and sample preparation

The Baxxodur® system 5300 (BASF The Chemical Company) was used in this study as epoxy matrix. It represents a two-component system using Baxxores® ER 5300 as the resin monomer and Baxxodur® EC 5310 as the hardener. The graphene oxide filler was supplied by GARMOR. It is 5-10% edge oxidized, and each powder grain consists of ~10 graphitic layers, with an average particle diameter of 500 nm.
The resin was heated up to 55 ºC for several minutes prior to any sample manufacturing in order to ensure than there was no solidification and then left in a fume cupboard under ambient conditions to cool down slowly. A solvent method was used in order to finely disperse the filler inside the epoxy matrix. The organic solvent used was acetone and the obtained solution was 5 mg GO/mL. The nanofiller contents varied between 0.5 and 2 wt%. The monomer epoxy was added to the acetone/GO solution and then probe sonicated (UP 200S) for 3 h. The solvent was later removed by evaporation using a hot plate at 80 ºC for 1 h, under slow stirring. The procedure continued with vacuum degassing to ensure that no solvent was left inside the system. Along with the nanocomposite and the neat epoxy samples, a reference sample was also prepared. The reason was to demonstrate that there was no impact of the solvent method on the behavior of the epoxy resin. While the neat epoxy sample was prepared just by magnetic stirring with the curing agent, the reference epoxy sample, despite being unfilled, was prepared using the same procedure as the nanocomposites, meaning that it was mixed with acetone, probe sonicated and dried before casting into the mould. After mixing the epoxy with the nanofiller, the hardener was added in a weight ratio of 10:2 (epoxy:hardener). The final mixture was vacuum degassed again and then vacuum transferred into moulds, appropriately prepared. The moulds were metallic plates with a Melinex® spacer (thickness ~200μm) sandwiched between them to determine the sample thickness, with a release agent (Easy-Lease™) applied prior to the assembly. In the case of tensile testing, the samples were cured in appropriate, dog-bone shaped rubber moulds. Finally, the samples were placed inside oven for curing at 70 ºC for 6 h and then left to cool down slowly. After that, the samples were stored inside desiccator, under vacuum.

Characterization methods

The morphology, as well as the dispersion level achieved were investigated using a Hitachi H 7000 transmission electron microscope (TEM). An RMC MT-7 ultramicrotome was used to cut the samples. The diamond knife used was a Diatome 35º and each sample section was ~90 nm thick.
Differential scanning calorimetry (DSC) was used in order to observe the effect of filler load on the glass transition temperature of the samples, as well as the effect of the preparation method on the epoxy resin. The system used was Perkin-Elmer DSC7, which was operating with Pyris software. A calibration with 4.5 mg high purity indium was done prior to the measurements. The samples were sealed into aluminium cans. The measurements included holding at 25 ºC for 5 min and then heating up to 120 ºC with a heating rate of 10 ºC/min. Subsequently, another hold at 120 ºC was done for 2 min. Cooling down to 25 ºC at the same rate was used afterwards, with a new hold at this temperature for 5 min, taking place. A second heating with the same rate was used in order to detect the T_g. The thermographs were normalized with the respective sample's weight, and then the T_g was determined, from the inflection point of the step like transition of the heat flow.
The electrical conductivity of the samples was measured using a Keithley 6487 picoammeter connected with an external voltage source. The sample holder was a capacitor-like arrangement with two circular gold coated electrodes of 20 mm diameter. The measurements were done using a ramp with a starting voltage of 100 V, a voltage step of 100 V and voltage application of 10 sec.
The Young modulus and tensile strength of the manufactured samples was determined using an Instron® 5569 with a load shell of 20 kN following the ASTM D638 – 02A. The samples were dog-bone shaped with a thickness of 4 mm each. The displacement rate was 1mm/min until sample failure.
A Rheolab® MC 1 rheometer of cylinder/cup configuration was deployed to monitor the viscosity of the nanocomposite systems at ambient temperature. Regarding the sample preparation, after the solvent was removed, the mixture temperature was elevated so they were kept under vacuum overnight to cool down. Afterwards, the systems were mixed with the hardener and vacuum degassed for 10 min, before measuring.

Results

The morphology of two nanocomposite samples can be found in Figures 1.1 and 1.2. The examined samples were the ones with 0.5 and 2 wt% of GO. As expected, the nanoparticles exhibit a great average distance between each other in the case of the low filler content. A smaller distance can be seen in the case of the high filler content, but still there are no contact points between the nanoparticles. The variation on the colour tone between different nanoflakes indicates an alteration of its thickness which can be associated with possible folding of a single sheet, or different sheets stacking on top of each other. Various sizes of GO flakes can be observed, with the average dimension observed being similar to the supplier's specified size.
Table 1.1 shows the variation of the glass transition for different filler contents. A small variation of the T_g can be seen and it suggests that there is an optimum filler content at 1 wt% and beyond that there is a small decrease. On the other hand, these variations fall into the error of the measuring apparatus

and can be considered negligible. It is apparent that the solvent did not had effect on the resin's response, as the reference sample exhibits similar T_g values with the neat epoxy sample.

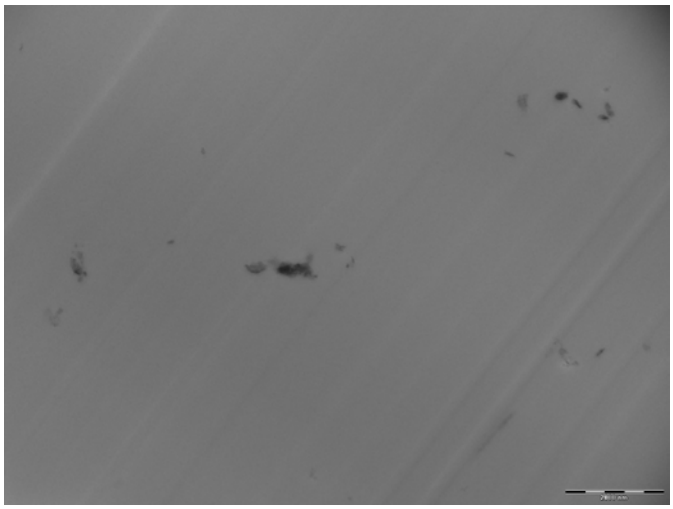

Figure 1: TEM image for the 0.5% wt GO (magnification x6000, scale bar 2 μm)

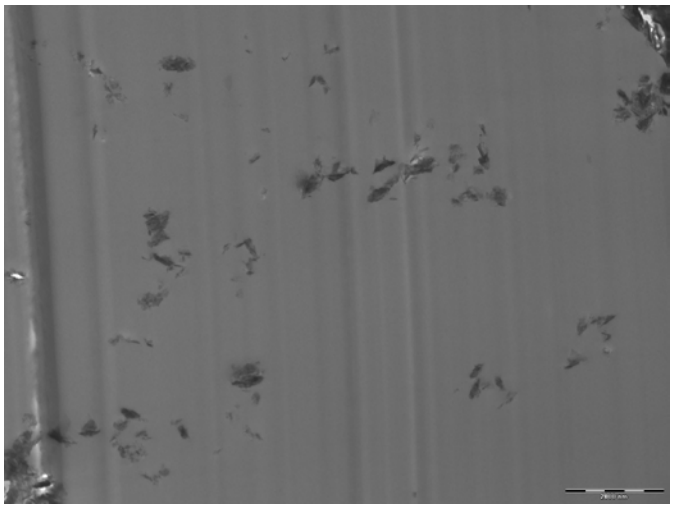

Figure 2: TEM image for the 2% wt GO (magnification x6000, scale bar 2 μm)

% wt GO	% vol GO	T_g (°C) (±2)
Neat epoxy	0	78.3
Reference	0	77.3
0.5	0.3	78.3
1	0.6	81.7
1.5	0.9	79.2
2	1.2	77.3

Table 1: The glass transition of the respective nanofiller contents in mass and volume ratios.

The current density versus the applied electric field for each sample can be seen in Figure 1.3. First, it can be observed that the neat and reference epoxy samples show similar behaviour, indicating that no solvent was trapped inside the system and thus, not effect on the conductivity occurred. It is also evident that the incorporation of small percentages (such as 0.5%) of GO does not result in any alterations of the conductivity. As the nanofiller content increases, the system's response changes accordingly. The incorporation of 2 wt% of GO leads to an increase of the conductive current passing through the material. Nevertheless, the TEM images suggest that no contact between the GO nanoflakes occurs at this filler content. It is assumed that the interparticle distance achieved is sufficient to increase the conductivity of the sample by several orders of magnitude.

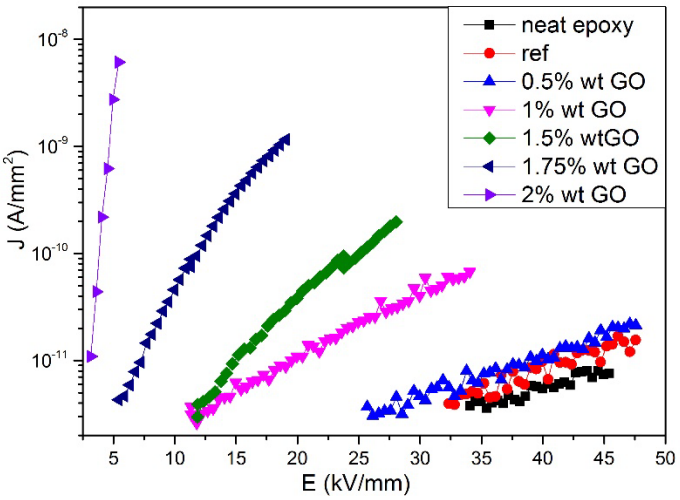

Figure 3: Current density versus applied electric field for all samples.

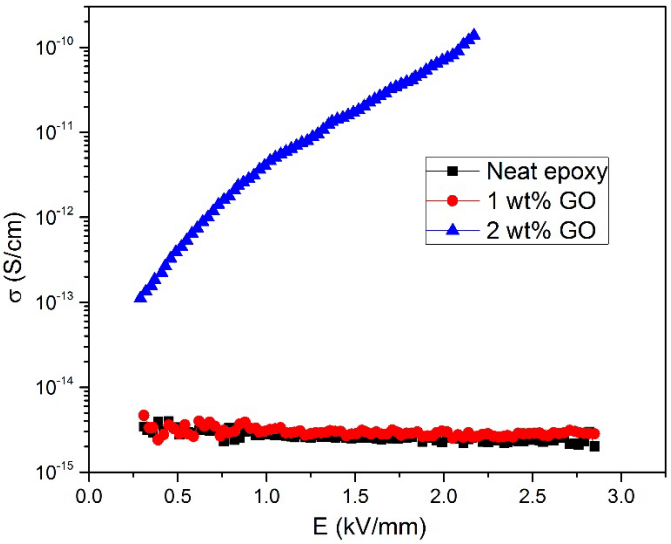

Figure 4: Electric field dependency of the conductivity for epoxy resin and two nanocomposite samples.

It can be seen (Figure 4) that in the case of the sample containing 2 wt% GO, there is a strong dependence of the electrical volume conductivity on the electric field. Although the sample is below percolation level (as indicated by TEM), a sub-percolation conductive path can be formed which

facilitates the charge transport as the applied electric field increases [13].
The Young's modulus and the stress to failure where measured for three nanocomposite samples as well as for the neat epoxy. The results are presented in Table 2. It can be seen that the incorporation of GO inside the epoxy has no adverse effects on its Young's modulus. More specifically, the low filler content slightly increases the Young's modulus, while further addition of GO reduces it to the initial neat epoxy values. The effect of the filler seems to slightly decrease the stress to failure, but the volume of the decrease falls in the deviation error. Since no effects of the solvent method were traced on properties like electrical conductivity and T_g, no reference sample was measured.

sample	E (GPa)	$\sigma_{fraction}$ (Mpa)
Neat epoxy	2.997 ± 0.160	75.08 ± 5.33
0.5 wt% GO	3.209 ± 0.110	76.61 ± 4.7
1 wt% GO	2.993 ± 0.036	68.3 ± 3.53
2 wt% GO	3.044 ± 0.057	70.55 ± 2.5

Table 2: The Young's Modulus and tensile strength of neat and nanocomposite epoxy resin.

The viscometric analysis was conducted, at ambient temperature, in order to investigate the viscosity of the mixture while on liquid state, after it was mixed with the solvent method (commercial GO). It can be observed in Figure 5 that there is a slight viscosity increase but no significant alterations.

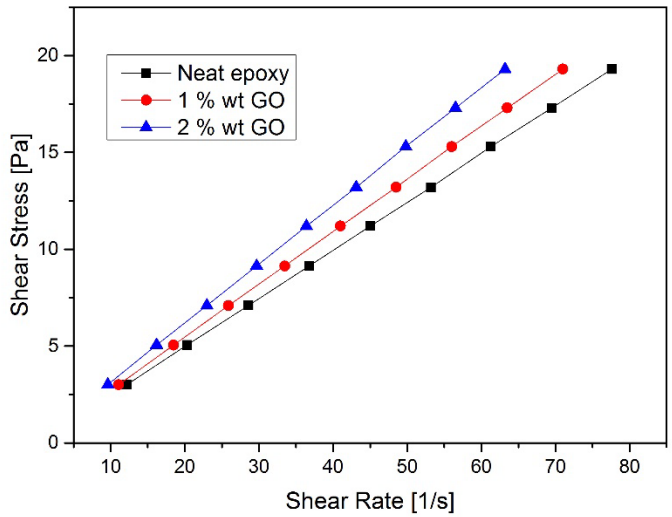

Figure 5: Viscometric analysis of the neat epoxy and two nanocomposite samples

The calculated viscosities are:

- 251 ± 1.2 mPa·s for the neat epoxy
- 271 ± 9.3 mPa·s for 1% wt GO filled
- 308 ± 1.4 mPa·s for 2% wt GO filled

These results align with the TEM images, suggesting that no contact between the filler was achieved, and thus the viscosity remained low. A low viscosity is very important for the processing of the material, especially for vacuum assisted resin transfer moulding.

Conclusions

Nanocomposite epoxy resin filled with conductive GO as a filler in different contents was prepared. It was found that the incorporation of 2 wt% of the filler is sufficient to increase the conductivity of the system, despite the fact that no contact points between the nanoflakes was achieved. The T_g of the system was not affected, keeping the maximum operation temperature at the same levels. The tensile tests showed a variation of the Young modulus dependent on the filler, with the optimum being in very low filler contents. Nevertheless, the Young modulus of the nanocomposite exhibiting high conductivity is maintained at the same values as the neat epoxy resin. The tensile strength of all the examined samples showed similar values. Finally, the viscosity of the samples did not show any significant alterations. The main objective of increased conductivity in low filler contents was fulfilled without compromising the mechanical, thermal and processing properties of the system, making the examined materials promising for applications in WT blade components using carbon fibres.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 642771.

The author would like to thank GARMOR for their generous supply of GO nanopowder.

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