Prediction method of electrical conductivity of nano-modified glass fibre reinforced plastics

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Abstract. Glass fibre reinforced plastics (GFRP) is non-conductive construction material, however with carbon nanotubes (CNT) modifying it can get additional functionality due to its gained electrical conductivity. Main aim of the study is to check functionality of the prediction method of electrical conductivity of GFRP with nano-modified epoxy matrix using structural approach. GFRP composites under investigation were based on unidirectional (UD) Glass fiber and two matrices modified with carbon nanotubes. Electrical conductivity of epoxy resin modified by CNT (concentrations < 1 %) was modelled using structural approach. Electrical conductivity of unidirectional GFRP layer was measured experimentally and modelled based on conductivity of polymer matrix and assuming non-conductive fibres. It was supposed that epoxy matrix and composite on different structural levels follow the Ohm’s law. Two components of tensor of electrical conductivity for monotropic material in main axis of symmetry were calculated for composites by several different ways. Control experiment was performed on a sample of GFRP monolayer cut from the unidirectional plate under different angles. The calculated data are in a good agreement with the experimental values.

1. Introduction
Glass fibre reinforced plastics (GFRP) is a construction material, that has grown within global market for 9% over last 5 years according to the world’s largest market research store “Research and markets” [1]. Being part of a composite, glass fibres stand for good mechanical properties of the whole system keeping it still 15-20% lighter than traditional metals. Owing to GFRP light weight, they are used as substitutes for steel and aluminium in various industries. GFRP is being originally electrical insulator, however, modifying matrix of GFRP with electrically conductive carbon nanotubes (CNT) makes the whole system improve its mechanical and electrical properties. The electrically conductive composites can be produced with high electrical conductivity at volume content of CNTs below 1%. Consequently, the carbon nanotubes are extending the usage range of GFRP with modified matrix in biomedical, electronic, automotive and aerospace industries [2]. Despite other modifications, with ability to control the electrical conductivity of GFRP rises potential of composite to detect structural damage of material (damage monitoring), screen the electromagnetic irradiation and drain electrostatic charging [3-7]. CNT-modified matrix is usually considered as an isotropic material and variety of models are applied for estimation of its electrical conductivity depending on the content of conductive fillers [8-10]. To define electric current density in composites, its anisotropic electrical conductivity and stacking sequence of the laminated plates should be taken into account. For that reason, finite element modelling (with high computational costs) could be applied to calculate electric current...
distribution in each subpart of the composite. Aside from this, electromechanical modelling [11] and analytical calculation of the electric function (with simplification for orthotropic materials) [6] are also used as an alternative. And yet, there is an issue with making the easiest and possibly the fastest method for GFRP electrical conductivity prediction.

From other side, structural approach is wide used in mechanics of composite (glass fibre reinforced plastics) for prediction of e.g. their elastic properties [12]. Main aim of the study is to check functionality of the prediction method of electrical conductivity of GFRP with CNT-modified epoxy matrix using structural approach.

2. Materials
Composite under investigation was GFRP based on unidirectional (UD) glass fibre (511 g/m²) and CNT modified epoxy matrix. During this study 2 polymer matrices were used for different samples:

1. Aradur 3486 epoxy resin + Araldite LY 1564 hardener with CNT masterbatch Epocyl™ R128-02 (Nanocyl). Epoxy resin was premixed with masterbatch during 20 min, later hardener was added and mixed 10 min more. Vacuum chamber was used for matrix degassing for 40 min. CNT concentration of 0.75 wt% was selected for polymer matrix to provide optimal combination of viscosity and conductivity of the matrix based on previous research [8, 13]. Vacuum bagging was used during 30 min to remove excess of the epoxy matrix before hardening. Hardening of nanomodified matrix, composite was performed in low vacuum at 50 °C during 24 h. Final size of samples was 200×150×3 mm. Considering the reinforcement coefficient 0.8 (by mass) of final composite, its CNT concentration is 0.15 wt%.

2. Nano-Force® E200 epoxy resin (masterbatch) contains less than 0.7 wt% CNT (the exact amount of CNT was not specified by the manufacturer) + E hardener system. Epoxy resin and hardener were mixed in 100 : 30 ratio for 10 min at the room temperature of about 20 °C. After the mixing, prepared epoxy system contained less than 0.5 wt% CNT. Composite production steps were identical to previous sample type. Final size of samples was 200×150×3 mm. Considering the reinforcement coefficient 0.55 (by mass) of prepared composite, its CNT concentration is estimated less than 0.2 wt%.

UD plates consist of 8 UD layers [0°]s with fibre direction oriented along axis 1. Reinforcement coefficient of UD plates and laminates was 0.7 (Epocyl™ 128-02) and 0.47 (Nano-Force®) by volume. Samples of the composite for measurements of components of resistivity tensor in main axis of symmetry of the material were strip shape with sizes 70×10×3 mm cut along and across fibre directions (in directions 1 and 2, respectively). Resistivity measurements were performed along 70 mm side. Samples for measurement of resistivity off-axes were square plates 60×60×3 mm with fibre orientation 45° to square sides.

Cross ply symmetrical composite laminates consisted totally of 8 UD layers [0/90]s. Plate sizes were 190×140×2.6 mm. Resistivity measurement were performed in both in-plane directions. Control experiment was performed on plate of 60×60×2.6 mm cut under 45° (only for Epocyl™ R128-02) to the composite main axes of symmetry.

Typically, 3 to 5 samples were tested in most of experiments and average data with standard deviation are presented in figures. Exception were two control samples with orientation 45°.

Resistance was measured by two-electrode method on direct current within linear segment of voltage-current dependence (that follows Ohm’s law) up to 40 V. Silver paste contacts were created on opposite faces of samples and cover all its surfaces. DMM4020 Digital Multimeter by Tektronix, Inc. was used for voltage measurements with resolution 100 μV in range up to 20 V. Laboratory Power Supply PS 200 B by Elektro-Automatik GmbH was used for power supply that provides DC stability better than 0.02 %.
3. Modelling of composite electrical conductivity

3.1. Micro-scale
Fibre reinforced UD composite in micro-scale could be considered as a set of long parallel fibres placed in a polymer matrix. Tensor of electrical conductivity of this monotropic material in main axis of symmetry could be written as

\[
s_0 = \begin{pmatrix}
s_{11} & 0 & 0 \\
0 & s_{22} & 0 \\
0 & 0 & s_{33}
\end{pmatrix}
\]

(1)

If fibre direction is along axis 1, one can assume that \( s_{22} = s_{33} \) and only two independent components of the tensor fully characterise the material. Components of the tensor for UD GFRP monolayer \( s_{11} \) and \( s_{22} \) could be calculated using conductivity of its structural components: matrix (superscript “m”) and fibre (superscript “f”). Rule of mixture (ROM) is the most reasonable to calculate longitudinal component of conductivity. Several equations could be used for calculation of transversal component similarly as it is accepted in calculation of thermal conductivity, diffusivity, e.g. [12]

\[
s_{11} = \eta s_{1f} + (1 - \eta)s_{mm}, \quad s_{22} = s_s = \left[1 + \frac{\eta}{s_{mm} \times (s_{1f} - s_{mm}) + (1 - \eta)l/2}\right]
\]

(2)

3.2. Macro-scale: monolayer
Sample of UD composite could be cut off main axes. In this case coordinate axis are rotated in plane 1–2 on angle \( \theta \) and the tensor components are transformed as

\[
s'_{ij} = \begin{pmatrix}
s'_{11} & s'_{12} & 0 \\
s'_{21} & s'_{22} & 0 \\
0 & 0 & s'_{33}
\end{pmatrix}
\]

(3)

where \( s'_{ij} = s_0 \cos(\alpha_i) \cos(\alpha_j) \) and \( \alpha_{22} = \alpha_{11} = \theta \). Respectively for this case:

\[
s'_{11} = s_{11} \cos^2 \theta + s_{22} \sin^2 \theta, \quad s'_{22} = s_{11} \sin^2 \theta + s_{22} \cos^2 \theta,
\]

(4)

\[
s'_{12} = s'_{21} = (s_{22} - s_{11}) \sin \theta \cos \theta \]

(5)

\[
s'_{33} = s_{33}.
\]

(6)

Let us consider a specific case for a sample cut with \( \theta = 45^\circ \). In-plane tensor components could be calculated using equations:

\[
s'_{11} = \frac{1}{2} (s_{11} + s_{22}), \quad s'_{22} = \frac{1}{2} (s_{22} + s_{11}), \quad s'_{12} = \frac{1}{2} (s_{22} - s_{11}).
\]

(7)

It follows from equation (7) that for \( \theta = 45^\circ \) in-plane components of conductivity are equal to average value of both components in main axes.

3.3. Macro-scale: laminate with symmetrical layup
A set of stacked UD layers creates a laminate and is the most interesting for practical application. Two specific cases of symmetric layup \([0/90^\circ]_n\) and \([\pm \theta]_n\) are presented in Figure 1.
Figure 1. Macro-scale of composite with symmetrical layup with orientation of layers 0/90°, ±θ.

If a lamina of thickness $H$ consists of $N$ layers’ conductivity may be calculated using expression

$$S'_{ii} = \frac{1}{H} \sum_{i=1}^{N} h_{i} s'_{ii(i)} (8)$$

In-plane conductivities 11 and 22 can be written as

$$S'_{11} = \frac{1}{H} \sum_{i=1}^{N} h_{i} (s_{11} \cos^2 \theta_{(i)} + s_{22} \sin^2 \theta_{(i)}) (9)$$

$$S'_{22} = \frac{1}{H} \sum_{i=1}^{N} h_{i} (s_{11} \sin^2 \theta_{(i)} + s_{22} \cos^2 \theta_{(i)}) (10)$$

Let’s consider two specific cases of symmetrical layup:

1. The first one, $\theta = 0/90^\circ$ layup

$$S'_{11} = \frac{1}{2} (s_{11} + s_{22}) \ , \ S'_{22} = \frac{1}{2} (s_{22} + s_{11}) (11)$$

2. The second case, layup with orientation of layers $\theta = \pm 45^\circ$. This gives expressions

$$S'_{11} = \frac{s_{11}}{H} \sum_{i=1}^{N} h_{i} \cos^2 \theta_{(i)} + \frac{s_{22}}{H} \sum_{i=1}^{N} h_{i} \sin^2 \theta_{(i)} (12)$$

$$S'_{22} = \frac{s_{11}}{H} \sum_{i=1}^{N} h_{i} \sin^2 \theta_{(i)} + \frac{s_{22}}{H} \sum_{i=1}^{N} h_{i} \cos^2 \theta_{(i)} (13)$$

Simplify we will get similar to equation (11):

$$S'_{11} = \frac{1}{2} (s_{11} + s_{22}) (14)$$

$$S'_{22} = \frac{1}{2} (s_{22} + s_{11}) (15)$$

$$S_{33} = s_{33} = s_{22} (16)$$

$$S_{12} = S_{21} = 0 (17)$$

4. Experimental results and discussion

Two components of the tensor were experimentally measured and it was determined that the degree of anisotropy (ratio of the tensor components) is higher than one order of magnitude. Tensor components of resistivity $s_{11}$ and $s_{22}$ for non- and reinforced samples are shown in Figure 2.
Due to anisotropy of reinforced modified polymer matrices, untypical data of conductivity of fibres $s_{11}'$ and $s_{22}'$ was supposed for calculations to avoid discrepancy in conductivity of the components and composite, and may be considered as some effective characteristic of the component but not of fibre material – glass itself. Possible reason of this discrepancy may be difference in bulk and micro conductivity of the components and boundary layer of matrix, but this is a point of interest for further experimental research and modelling.

Calculated and experimental data for nanomodified composites based on Epocyl™ and Nano-Force® masterbatches for all cases are presented in Figure 3.

Conductivity for composite based on Epocyl™ 128-02 is greatly higher than for Nano-Force® E200 one. These are different materials from two manufacturers and CNT concentrations are different. CNT concentration of polymer matrix for Epocyl™ 128-02 based composite is higher than for Nano-Force® E200 one. More detailed investigation is needed for in-depth understanding of composite reinforcement-conductivity correlation.

Despite the strong conductivity difference of tested materials, the calculated data are in a good agreement with the experimental values for both composites within small and high CNT concentration range.
5. Conclusions
The effective electrical conductivity of the matrix and composites were determined experimentally. Anisotropy due to orientation of non-conductive fibers was taken into account by introducing the corresponding anisotropic conductivity tensor for each ply. Measurements of electrical conductivity were made for unidirectional single- and multi-ply composites cut on various angles, as well as for orthotropic cross-ply GFRP laminates. The experimental and calculated data for both polymer matrices is in reasonable agreement, thus prediction method based on structural approach can be used for GFRP electrical conductivity calculating. Additional functionality of the composite could be used for monitoring of damage in the GFRP lamina with CNT-doped polymer matrix via electrical conductivity methods and their application for non-destructive in-service integrity monitoring of multifunctional composite panels in constructions.

Acknowledgments
Authors thank technician Viktor Novikov for sample preparation. The research leading to part of these results has received the funding from European Regional Development Fund project. ERDF project identification No.: 1.1.1.1/16/A/141.

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