STRUCTURAL APPROACH FOR PREDICTION OF ELECTRICAL CONDUCTIVITY OF NANO-MODIFIED GLASS FIBRE REINFORCED PLASTICS

A. Aniskevich, S. Stankevich, and J. Sevcenko

Institute for Mechanics of Materials, University of Latvia,
23 Aizkraukles str., Riga, LV-1006, Latvia
Andrey.Aniskevich@pmi.lv, obis8053@gmail.com,
http://www.pmi.lu.lv/

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Abstract

Modified glass fibre reinforced plastics (GFRP) with carbon nanotubes (CNT) can get additional functionality that opens a prospective for use in a wide range of high-performance applications as also possess ability to damage monitoring via control of electrical conductivity. Main aim of the study is to predict electrical conductivity of GFRP with CNT-modified epoxy matrix using structural approach.

Electrical conductivity of epoxy resin modified by CNT (< 1%) was modelled using micro-structural approach. Electrical conductivity of unidirectional GFRP layer was modelled and measured experimentally. Two components of tensor of electrical conductivity for monotropic material in main axis of symmetry were calculated. Conductivity of a lamina consisting of *N* layers was calculated for symmetrical layup with orientation of layers $\pm\theta$.

Control experiment was performed on a sample of GFRP monolayer cut from the unidirectional plate under different angles. Experimental verification was performed for 8-layer GFRP with symmetrical layup $[0/90]_4$. The calculated data are in a good agreement with the experimental values.

1. Introduction

Glass fiber reinforced plastics (GFRP) is a construction material being originally electrical insulator. However, modifying matrix of GFRP with electrically conductive carbon nanotubes (CNT) makes the whole system significantly improve its mechanical and electrical properties. The electrically conductive composites can be produced with high electrical conductivity at volume content of CNTs below 1% [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 [1, 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 method (with high computational costs) is applied to calculate electric current distribution in each subpart of the composite. Aside from this method, 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 widely used in mechanics of composite (e.g. GFRP) for prediction of their elastic properties [12]. The main aim of this study was to analyze and check applicability of structural mechanical approach for prediction of electrical conductivity of GFRP with CNT-modified epoxy matrix.

2. Materials

Composite under investigation was unidirectional (UD) GFRP based on UD Glass fibre (511 g/m^2) and CNT modified epoxy matrix. Polymer matrix used was Araldite LY 1564 + Aradur 3486 epoxy resin with CNT from masterbatch Epocyl NC R128-02. Masterbatch was premixed with epoxy resin during 20 min and later hardener was added and mixed during 10 min more. Matrix was degassed in vacuum chamber during 40 min. CNT content in the polymer matrix changes from 0.3 to 1.5 % in previous research [1, 8, 13], but was constant 0.75 % in the given part of research thus providing optimal combination of viscosity and conductivity of the matrix. Hardening of nanomodified matrix and composite was performed in low vacuum at temperature 50 °C during 24 h. Samples of epoxy matrix after hardening had a form of plate with sizes 200×150×3 mm and in-plane resistivity measurements were performed along 200 mm side. GFRP composites were hand-made layup and vacuum bagging during 30 min to remove excess of the epoxy matrix.

UD plates consist of 8 UD layers $[0°]_8$ with fibre direction oriented along axis 1. Reinforcement coefficient of UD plates and laminates was 0.7 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 $[0/90]_4$ with orientation 0 and 90°. 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° 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 on figures. Exceptions 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. Nanomodified polymer matrix

Electrical conductivity of Araldite + Aradur epoxy resin strongly depends on CNT concentration (Figure 1) and was investigated earlier [1, 8, 13].

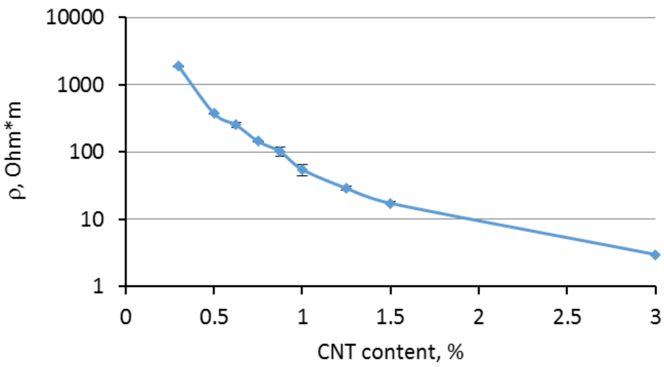

Figure 1. Resistivity of epoxy matrix modified with different content of CNT. Standard deviation error bars are hardly visible in semi-logarithm plot.

From one hand, resistance of nanomodified matrix drops on several orders of magnitude that makes the matrix electrically conductive material with reasonable resistivity ca. 10-100 Ohm·m. From other hand, growth on CNT concentration essentially increases viscosity of the matrix thus limiting the use of the nanomodified polymer resin as a composite matrix. Taking into account both considerations, Araldite + Aradur epoxy system with fixed concentration of CNT 0.75 % and conductivity $s^m = (1.7 \pm 0.2)\cdot 10^{-3}$ S/m was used in this research (superscript "m" relates to polymer matrix).

4. Composite

4.1. 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

$$s_{ij} = \begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{22} & 0 \\ 0 & 0 & s_{33} \end{pmatrix} \tag{1}$$

If fibre direction is along axis 1, one can assume that $s_{22} = s_{33}$ and only two independent component of the tensor fully characterise the material. 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.

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]

$$s_{11} = \eta s_{11}^f + (1-\eta)s^m\,,\; s_{22} = s^{\mathrm{m}}\left[1 + \frac{\eta}{s^{\mathrm{m}}/(s_{22}^f - s^m) + (1-\eta)/2}\right] \tag{2}$$

Input data and results of calculation are given in Figure 3. Untypical data of conductivity of fibres s_{11}^{f} and s_{22}^{f} 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.

4.2. Macro-scale: monolayer

Let's consider a sample of UD composite cut off main axes of symmetry. In this case coordinate axis are rotated in plane 1–2 on angle θ and the tensor components are transformed as

$$s'_{kl} = \begin{pmatrix} s'_{11} & s'_{12} & 0 \\ s'_{21} & s'_{22} & 0 \\ 0 & 0 & s'_{33} \end{pmatrix} \tag{3}$$

where $s'_{kl} = s_{ij}\cos(\alpha_{ki})\cos(\alpha_{lj})$ and $\alpha_{2'2} = \alpha_{1'1} = \theta$. Respectively for this case:

$$s'_{11} = s_{11}\cos^2\theta + s_{22}\sin^2\theta\ ,\ s'_{22} = s_{11}\sin^2\theta + s_{22}\cos^2\theta\ , \tag{4}$$

$$s'_{12} = s'_{21} = (s_{22} - s_{11})\sin\theta\cos\theta,\ s'_{33} = s_{33}$$

Let us consider a specific case for a sample cut with θ = 45°. In-plane tensor components could be calculated using equations

$$s'_{11} = \frac{1}{2}(s_{11} + s_{22})\ ,\ s'_{22} = \frac{1}{2}(s_{22} + s_{11})\ ,\ s'_{12} = \frac{1}{2}(s_{22} - s_{11}) \tag{5}$$

It follows from (5) that for θ = 45° in-plane components of conductivity are equal to average value of both components in main axes. Result of calculation are given in Figure 3 with legend UD composite cut under θ = 45° (UD45 s'_{11} and UD45 s'_{22}).

4.3. 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 layer orientation 0/90° and $\pm\theta$ are presented in Figure 2.

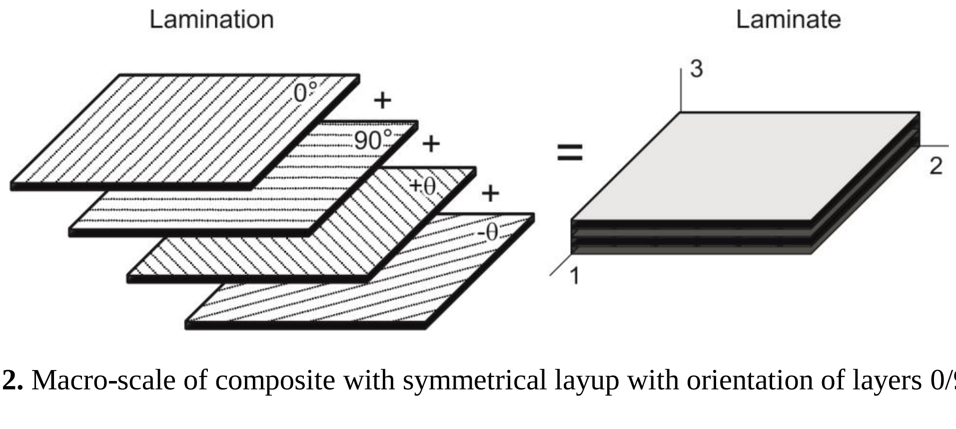

Figure 2. Macro-scale of composite with symmetrical layup with orientation of layers 0/90°, ±θ.

If a lamina of thickness H consists of N layers', its conductivity may be calculated using expression

$$S'_{kl} = \frac{1}{H}\sum_{i=1}^{N} h_i s'_{kl(i)} \tag{6}$$

In-plane conductivities 11 and 22 can be written as

$$S'_{11} = \frac{1}{H}\sum_{i=1}^{N} h_i (s_{11}\cos^2\theta_{(i)} + s_{22}\sin^2\theta_{(i)}) \text{ and } S'_{22} = \frac{1}{H}\sum_{i=1}^{N} h_i (\sin^2\theta_{(i)} + s_{22}\cos^2\theta_{(i)}) \tag{7}$$

Let's consider two specific cases of symmetrical layup.

The first case, θ = 0/90° layup

$$S'_{11} = \frac{1}{2}(s_{11}+s_{22}) \text{ , } S'_{22} = \frac{1}{2}(s_{22}+s_{11}) \text{ ,} \tag{8}$$

The second case, layup with orientation of layers θ = ± 45°. This gives expressions

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

Simplify we will get similar to (8)

$$S'_{11} = \frac{1}{2}(s_{11}+s_{22}) \text{ , } S'_{22} = \frac{1}{2}(s_{22}+s_{11}) \tag{9}$$

$$S_{33} = s_{33} = s_{22} \text{ , } S_{12} = S_{21} = 0$$

Result of calculations for both specific cases $[0/90°]_4$ and $[\pm45°]_4$ are given in Figure 3. The calculated data are in a good agreement with the experimental values of the second control experiment.

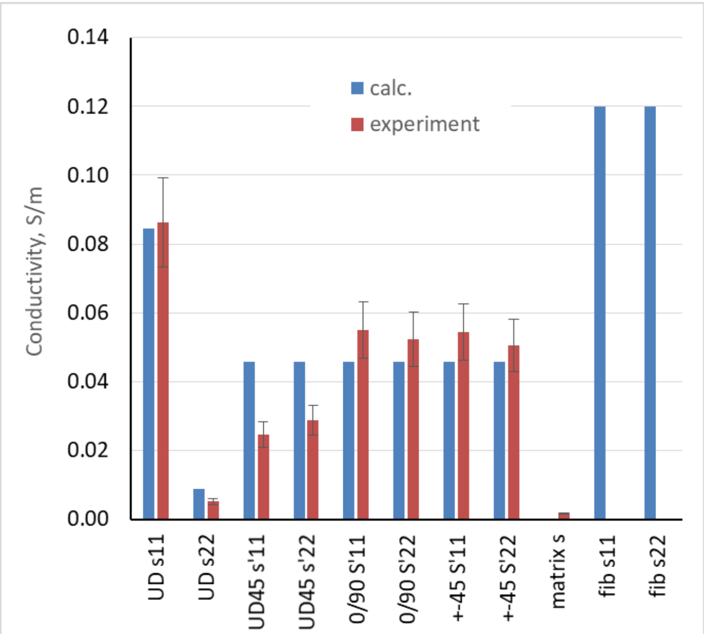

Figure 3. Experimental and calculated data of conductivity of CNT modified polymer matrix, UD composite in main axes (UD s_{11} and UD s_{22}), UD composite cut under θ = 45° (UD45 s'_{11} and UD45 s'_{22}), cross ply $[0/90°]_4$ laminate (S'_{11} and S'_{22}), and laminate $[\pm45°]_4$ (S'_{11} and S'_{22}), fibers (s_{11} and s_{22}).

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 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 are in reasonable agreement. 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.

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References

[1] A. Aniskevich, V. Kulakov, *Electrical Conductivity of Unidirectional Glass Fi-bre Reinforced Composite with CNT-Modified Epoxy Matrix*, ECCM17 - 17th European Conference on Composite Materials, Munich, Germany, 2016, pp. PO-2-54.
[2] P.R. Bandaru, *Electrical properties and applications of carbon nanotube structures*, Journal of nanoscience and nanotechnology, 7 (2007) 1239-1267.
[3] C. Viets, S. Kaysser, K. Schulte, *Damage mapping of GFRP via electrical resistance measurements using nanocomposite epoxy matrix systems*, Composites Part B: Engineering, 65 (2014) 80-88.
[4] R. Haj-Ali, H. Zemer, R. El-Hajjar, J. Aboudi, *Piezoresistive fiber-reinforced composites: A coupled nonlinear micromechanical–microelectrical modeling approach*, International Journal of Solids and Structures, 51 (2014) 491-503.
[5] A.S. Liberson, B.R. Walsh, M.J. Roemer, G.P. Tandon, R.Y. Kim, I.T.L.R. NY., *Damage Quantification in Electrically Conductive Composite Laminate Structures*, Defense Technical Information Center2009.
[6] T. Yamane, A. Todoroki, *Analysis of electric current density in carbon fiber reinforced plastic laminated plates with angled plies*, Composite Structures, 166 (2017) 268-276.
[7] A. Naghashpour, S. Van Hoa, *A technique for real-time detecting, locating, and quantifying damage in large polymer composite structures made of carbon fibers and carbon nanotube networks*, Structural Health Monitoring, 14 (2014) 35-45.
[8] V. Kulakov, A. Aniskevich, S. Ivanov, T. Poltimae, O. Starkova, *Effective electrical conductivity of carbon nanotube–epoxy nanocomposites*, Journal of Composite Materials, 51 (2017) 2979-2988.
[9] G. Georgousis, C. Pandis, A. Kalamiotis, P. Georgiopoulos, A. Kyritsis, E. Kontou, P. Pissis, M. Micusik, K. Czanikova, J. Kulicek, M. Omastova, *Strain sensing in polymer/carbon nanotube composites by electrical resistance measurement*, Composites Part B: Engineering, 68 (2015) 162-169.
[10] P. Rajinder, *On the Electrical Conductivity of Particulate Composites*, Journal of Composite Materials, 41 (2007) 2499-2511.

[11] J.B. Park, T. Okabe, N. Takeda, W.A. Curtin, *Electromechanical modeling of unidirectional CFRP composites under tensile loading condition*, Composites Part A: Applied Science and Manufacturing, 33 (2002) 267-275.
[12] R.M. Christensen, *Mechanics of Composite Materials*, Dover Publications2012.
[13] V.L. Kulakov, A.N. Aniskevich, T. Poltimae, *Effective electrical conductivity of CNT-epoxy nanocomposites*, 20th International Conference on Composite Materials (ICCM-20), Copenhagen, Denmark, 2015, pp. paper-150701-151765.