STRUCTURAL MECHANIC APPROACH FOR PREDICTION OF ELECTRICAL CONDUCTIVITY OF GLASS FIBRE REINFORCED COMPOSITE WITH CNT-MODIFIED EPOXY MATRIX

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Keywords: GFRP, Electrical conductivity, Carbon nanotube, Micromechanics, Laminate

ABSTRACT

The electrical conductivity of GFRP cross-ply laminates with CNT-modified epoxy matrix was studied. The effective electrical conductivity of the matrix and composites were measured 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 are in reasonable agreement. Damage detection in GFRP with electrically conductive matrix was realized measuring the voltage distribution of the samples before and after damage and the analysis of damage correlated relative voltage changes. The results indicate that even a relatively large spaced electrode network is capable of determining location and quantification of damage.

INTRODUCTION

Incorporation of electrically conductive fillers, e.g. carbon nanotubes (CNT), into polymer matrixes of advanced fibre reinforced plastics allows one to get structural composites with the improved mechanical performance and tailored electrical conductivity. Glass fibre reinforced plastics (GFRP) being originally electrical insulators get additional functionality that opens a prospective for use in a wide range of multifunctional and high-performance applications, e.g. civil engineering, aerospace, and automotive industries [1], [2]. By adding of less than 0.3-0.7 wt.% of CNT into the polymer matrix, these composites possess ability to strain and damage monitoring via control of electrical conductivity [3]-[9]. CNT-modified matrix is usually considered as an isotropic material and variety of mixing and micromechanical models are applied for estimation of its electrical conductivity depending on the content of conductive fillers [10]-[12]. Laminated composites have an anisotropic electric conductivity, and the electric current density distribution is characterised by rather complicated configuration depending on the stacking sequence of the laminated plate. Finite element methods are usually applied for calculation of the electric current distribution in each ply, although often at a high computational cost. Alternative methods are based on electromechanical modelling [13] or analytical calculation of the electric potential function that can be simplified for the case of orthotropic materials [6], [8]. Despite on high interest on using CNT-doped GFRP as multifunctional damage-sensing structural composites, reliable estimation of electrical conductivity in these anisotropic composites is still an issue.

The main aim of the study is to check applicability of structural mechanic approach to prediction of electrical conductivity of GFRP with epoxy matrix modified by CNT and to check a possibility for damage detection of the composite using in-plane electrical voltage measurements.

It is supposed that epoxy matrix and composite on different structural levels obeys the Ohm's law and the electric flux density $\vec{j}$ is proportional to the electrical field $\vec{E}$

$$\vec{j} = \mathbf{s}\vec{E} \tag{1}$$

where ***s*** is a tensor of electrical conductivity. That means the electric current in the material with different degree of anisotropy can be regarded as an ideal flow in isotropic media and potential functions of perfect flow could be used for analysis of electric current [8].

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 [4, 10, 14], 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 with fibre direction oriented along axis 1 i.e. $[0°]_8$. 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 with orientation 0 and 90° i.e. $[0/90]_4$. 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. Exception were two control samples with orientation 45°.

Resistance was measured on direct current within linear segment of voltage-current dependence (that follows Ohm's law) up to 40 V. 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 %.

NANOMODIFIED POLYMER MATRIX

Electrical conductivity of epoxy resin modified by CNT was investigated earlier [e.g. 4, 10, 14]. Electrical conductivity of the Araldite + Aradur epoxy system strongly depends on CNT concentration as shown in Fig. 1.

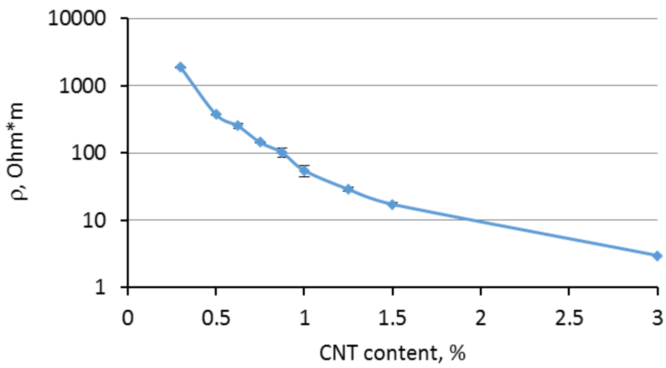

Figure 1: Resistivity of epoxy matrix modified with different content of CNT. Standard deviation error bars are hardly visible in semi-logarithm plot.

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 $(1.7 \pm 0.2)\cdot 10^{-3}$ S/m was used in this research.

MICRO-SCALE OF COMPOSITE STUDYING

Fibre reinforced UD composite in micro-scale could be considered as a set of long parallel fibres placed in polymer matrix as illustrated in scheme Fig. 2.

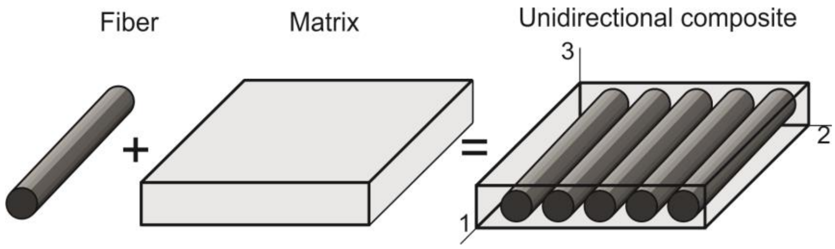

Figure 2: Micro-scale of UD composite.

This is monotropic material and its tensor of electrical conductivity in main axis of symmetry could be written as

$$s_{ij} = \begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{22} & 0 \\ 0 & 0 & s_{33} \end{pmatrix} \tag{2}$$

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. Both components of resistivity are shown in polar plot Fig. 3 with logarithm of resistivity by radius.

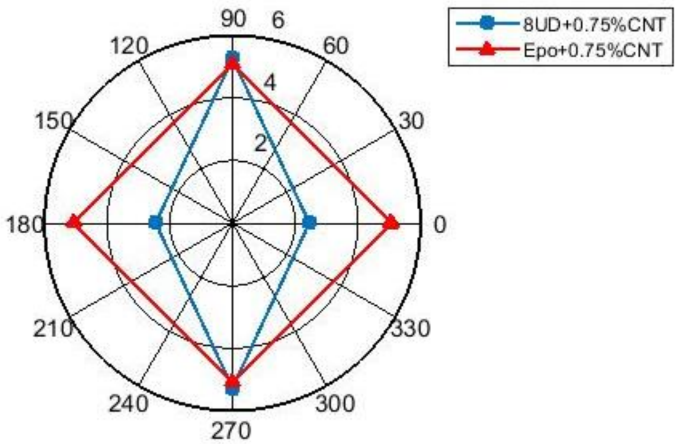

Figure 3: Polar plot of resistivity of monotropic composite (squares) and matrix with 0.75% of CNT (triangles). Radius is logarithm of resistivity (ln ρ, Ohm·m).

Components of the tensor for UD GFRP monolayer s_{11} and s_{22} could be calculated using conductivity of 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. [15, 16]

$$s_{11} = \eta s_{11}^{\mathrm{f}} + (1-\eta) s^{\mathrm{m}},\ s_{22} = s^{\mathrm{m}} \left[1 + \frac{\eta}{s^{\mathrm{m}} / (s_{22}^{f} - s^{m}) + (1-\eta)/2} \right], \tag{3}$$

Input data and results of calculation are given in Fig. 6. 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.

MACRO-SCALE OF COMPOSITE FOR SYMMETRICAL LAYUP

MONOLAYER

Sample of UD composite could be cut off main axes. In other words, that means coordinate axis are rotated in plane 1–2 on angle θ. The tensor components in this case are transformed as

$$s'_{kl} = \begin{pmatrix} s'_{11} & s'_{12} & 0 \\ s'_{21} & s'_{22} & 0 \\ 0 & 0 & s'_{33} \end{pmatrix} \tag{4}$$

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

$$s'_{11} = s_{11} \cos^2\theta + s_{22} \sin^2\theta,\ s'_{22} = s_{11} \sin^2\theta + s_{22} \cos^2\theta, \tag{5}$$

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

Dependence of relative conductivity $s'_{11rel} = (s_{\theta} - s_{22}) / (s_{11} - s_{22})$ on angle θ between fibre orientation and perpendicular to the sample surface is given in Fig. 4. The relative conductivity gradually changes its value from 1 to 0 as it could be expected.

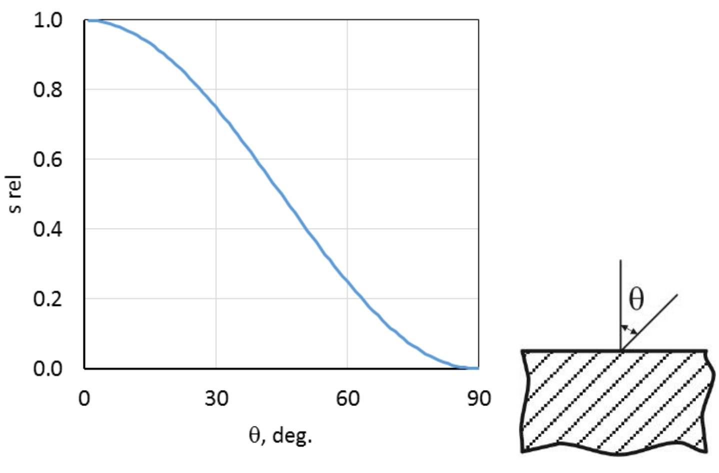

Figure 4: Dependence of relative conductivity on angle of reinforcement.

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

$$s'_{11} = \frac{1}{2}(s_{11} + s_{22}),\ s'_{22} = \frac{1}{2}(s_{22} + s_{11}),\ s'_{12} = \frac{1}{2}(s_{22} - s_{11}) \tag{6}$$

It follows from (6) and Fig. 4 that for $\theta = 45°$ in-plane components of conductivity are equal to average value of both components in main axes. Result of calculation are given in Fig. 6 with legend UD composite cut under $\theta = 45°$ (UD45 s'_{11} and UD45 s'_{22}).

LAMINATE

A set of stacked UD layers creates a laminate and is the most interesting. Two specific cases of symmetric layup $[0/90°]_n$ and $[\pm\theta]_n$ are presented in Fig. 5.

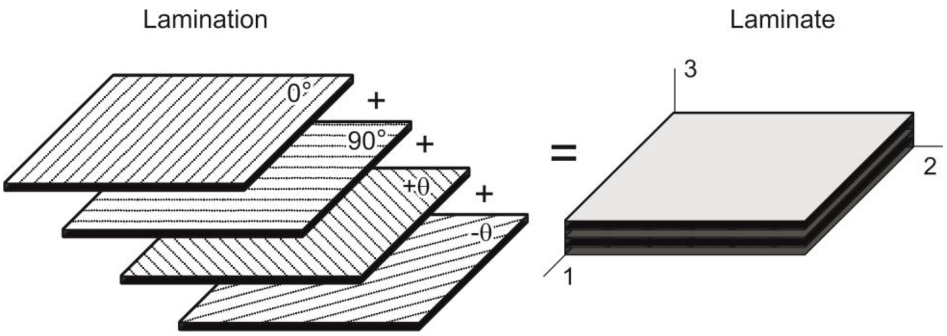

Figure 5: Macro-scale of composite for symmetrical layup with orientation of layers ±θ.

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

$$S'_{kl} = \frac{1}{H}\sum_{i=1}^{N} h_i s'_{kl(i)} \tag{7}$$

In-plane conductivities 11 and 22 can be written as

$$S'_{11} = \frac{1}{H}\sum_{i=1}^{N} h_i s'_{11(i)} \text{ and } S'_{22} = \frac{1}{H}\sum_{i=1}^{N} h_i s'_{22(i)} \tag{8}$$

Taking into account (5), (8) could be rewritten as

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

Let's consider two specific cases of symmetrical layup.

The first one, $\theta = 0/90°$ layup with $\sum_{i=1}^{N} h_{90(i)} = \sum_{i=1}^{N} h_{0(i)} = \frac{H}{2}$

$$S'_{11} = \frac{1}{2}(s_{11} + s_{22}),\ S'_{22} = \frac{1}{2}(s_{22} + s_{11}), \tag{10}$$

The second case, layup with orientation of layers $\pm\theta$ and $\sum_{i=1}^{N} h_{\theta(i)} = \sum_{i=1}^{N} h_{-\theta(i)} = \frac{H}{2}$. This gives expressions

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

Simplify

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

For $\theta = 45°$ we will get similar to (10)

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

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

Result of calculations for both specific cases [0/90°]$_4$ and [±45°]$_4$ are given in Fig. 6. The calculated data are in a good agreement with the experimental values of the second control experiment.

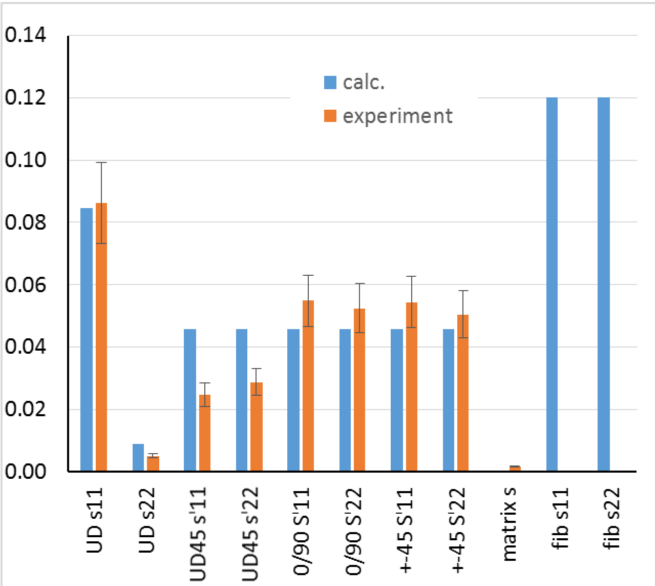

Figure 6: Experimental and calculated data of conductivity of CNT modified polymer matrix, UD composite in main axes (UD s_{11} and UD s_{22}), UD composite cut under $\theta = 45°$ (UD45 s'_{11} and UD45 s'_{22}), cross ply [0/90°]$_4$ laminate (S'_{11} and S'_{22}) and laminate [±45°]$_4$ (S'_{11} and S'_{22}), fibres (s_{11} and s_{22}).

DAMAGED COMPOSITE PLATE

Additional functionality of the composite was used for monitoring of damage in the GFRP lamina. This topic is of interest of many researchers, e.g. [9]. The GFRP plate [0/90]$_4$ of 20×20 cm had 8 rows by 8 point i.e. totally 64 silver coated contact points. Voltage of 20 V was applied to two adjacent corners of square plate. Two opposite end-planes with sizes 20×0.3 cm were used as silver coated electrodes but also their resistance was taken into account. Distribution of voltage was measured experimentally through a GFRP plate in a reference state. Voltage field on contact points by rows and columns of non-damaged plate is given in Table 1. Small changes of voltage along silver contact (row 8) is clear seen in the table.

Damage of the plate was simulated by a hole and a notch in the middle of the plate. Both these damages change voltage field on contact points of the plate in comparison with reference field and this difference (in V) is shown in Fig. 7.

	Voltage field on marker points, V							
	Point position number by column							
Point position number by row	1	2	3	4	5	6	7	8
1	19.92	19.92	19.92	19.92	19.92	19.92	19.92	19.92
2	13.75	13.64	13.73	13.9	14.01	14.52	13.99	14.02
3	10.82	10.79	10.87	10.91	10.78	11.07	11.38	11.26
4	9.54	9.38	9.41	9.43	9.41	9.57	9.77	9.7
5	7.96	7.86	7.74	7.49	7.54	7.84	7.8	7.76
6	6.24	5.91	5.78	5.76	5.6	5.55	5.61	5.65
7	3.69	3.6	3.6	3.43	3.46	3.43	3.69	3.82
8	0	0.002	0.004	0.006	0.008	0.01	0.012	0.014

Table 1: Voltage field on marker points by rows and columns of non-damaged plate.

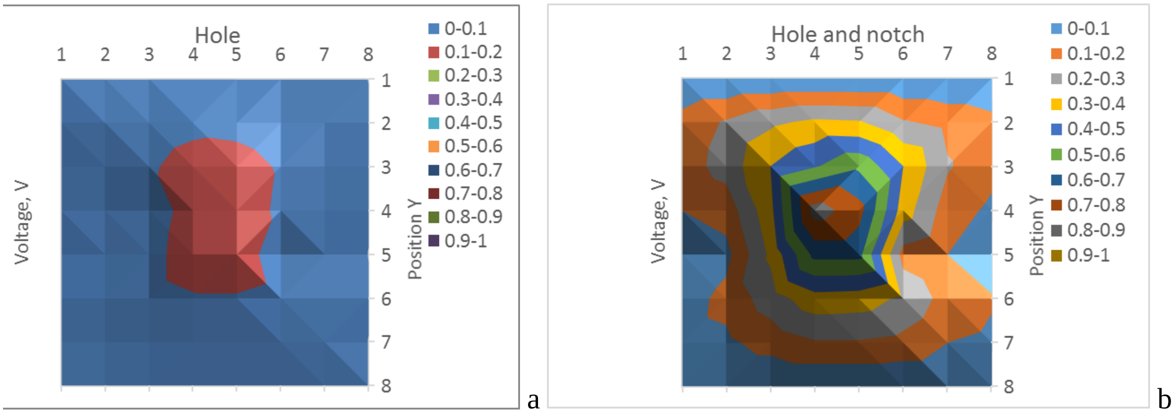

Figure 7: Changes of voltage distribution of damaged composite plate with hole (a) and hole-notch (b).

It was revealed an essential deviation of the potential distribution in the damaged state with respect to the reference one. The deviation was sensitive to the shape of damage. The obtained results demonstrate a possibility of damage detection in GFRP structures 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.

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 are in reasonable agreement. Damage detection was realized measuring the voltage distribution of the samples before and after onset of damage and the analysis of damage correlated relative voltage changes. The results indicate that even a relatively large spaced electrode network is capable of determining location and quantification of damage.

ACKNOWLEDGEMENTS

Authors thank technicians Viktor Novikov and Jevgenijs Sevcenko for sample preparation and measurements. The research leading to part of these results has received the funding from H2020 MSCA project SMARCOAT.

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