

Structure and Properties of SWCNT-Modified CFRP

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Abstract. Structure and mechanical properties of CFRP modified by SWCNT with different content (0.1, 0.2 and 0.3 wt. %) have been studied in the present paper. The structural investigations include SEM imaging while the mechanical properties have been characterized via tensile and flexural tests. The main functional feature of such hybrid composite is an electrical conductivity, which has been also measured. Out-of-plane conductivity has been enhanced up to ~66 S/m from dielectric unmodified CFRP. It has been shown that tensile properties stay almost unchanged, while flexural strength and modulus have increased by 22% and 16% correspondingly.

1. Introduction

In recent decades the application of composites in the industry was significantly increased due to their superior mechanical properties as well as an opportunity to obtain wide range of variation of these properties by producing composites with different constituents and contents in order to satisfy all requirements. In this case, the new trend in the composite manufacturing is hybrid composites, which together with conventional continuous fiber reinforcement applies dispersive nano- or micro- fillers. Due to such a technique it is possible to produce materials with completely new properties or enhance existing.

Concerning carbon fiber-reinforced composites (CFRP) used in the aerospace industry, a very promising way is an addition of single-wall (SW) or multi-wall (MW) carbon nanotubes (CNT) [1,2]. CNTs added to CFRP results in an increase in composite of electrical and heat conductivity, which could be useful for lightning protection and higher efficiency of de-icing systems. Similar results with some electromagnetic shielding effect could be obtained using metal powders [1,3,4,5]. Nanomaterials are much more expensive than microfillers, but it is shown in papers that micro-sized additives [6,7] can be successfully used for the manufacturing of hybrid fiber-reinforced polymers.

The described approach has a limitation in its industrial application due to a problem in a homogeneous dispersing of small-sized reinforcement in the matrix. One of the ways for solving the issue is ultrasound (US) assisted mixing, applicable in the laboratory or industrial environment [8,9].

The present paper is devoted to the laboratory investigation of the structure and the properties of CFRP filled with SWCNT using ultrasonic homogenization and manual layup.

2. Materials and methods

Hybrid CFRP/SWCNT specimens were prepared in order to investigate tensile and flexural strength and electrical conductivity. Single-wall carbon nanotubes used are provided by OcSiAl (Russia,



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Novosibirsk). SWCNT had a mean diameter of 1.6 ± 0.4 nm and a length of more than 5 μm . Epoxy resin of L grade and hardener CL were manufactured by R&G, Germany. This epoxy binder (L epoxy + CL hardener) can be used to produce medium-to-high performance CFRPs which have the properties comparable to CFRP made using aerospace approved binders. The carbon reinforcement used is 200 g/m² dense plain fabrics of Tenax® HTA 40/200 tex, 3k carbon fiber. VATI basalt plain fabrics of 200 g/m² were used in the middle of the stack allow avoiding the contact between neighboring carbon fiber layers and helping to investigate directly the effect of CNTs on electrical conductivity. The stacking sequence of $[(0/90_C)_4, (0/90_B)_2]_S$ results in a 2.1 mm thick 12-ply orthotropic laminate. Hand lay-up with hot pressing using Gotech 7014-R (pressure 0.48 MPa, heating of plates to 60 °C, and 12 hours post-cure) was used to fabricate blanks which were cut into specimens using milling machine. Table 1 and Figure 1 present the specimens investigated in the research.

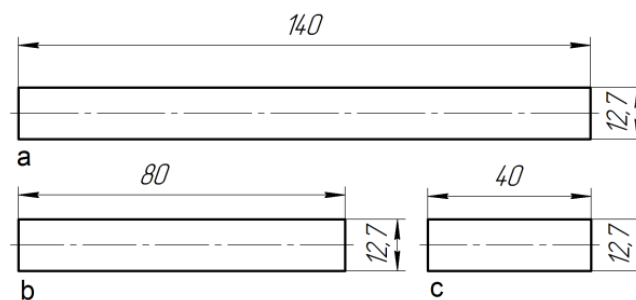


Figure 1. Sketches of the specimens for a) tension; b) 3-point bending; c) conductivity measurement.

The mixtures of epoxy and SWCNT were prepared by mechanical mixing during 1 minute and ultrasonication using UZDN-A (Russia) probe sonicator for 20 minutes with a frequency of 22 kHz and power of 130 W. During ultrasonic mixing the glass was constantly cooled in water. After cooling the hardener was added to the mixture that was used in the CFRP lay-up. Summary there were initial non-modified epoxy and 3 types of SWCNT-modified: with 0.1 wt.%, 0.2 wt.%, and 0.3 wt.% of SWCNT. In order to perform conductivity measurement of the CFRP specimens the tabs of silver conductive paint were prepared. The tabs were placed within a 30 mm distance and electrical conductivity was measured between these pads using LCR meter E7-20, Russia. There were 3 configurations for conductivity measurement: in-plane surface, out-of-plane diagonal, and out-of-plane through-thickness.

The specimens were tested using Instron 5582 universal testing machine. Quasi-static tension was performed at a rate of 1.5 mm/min with a gauge length of 70 mm. Three-point bending was conducted with a span of 60 mm at 10 mm/min rate. The initial structure and surfaces of fractured specimens were investigated by SEM using LEO EVO 50 (Zeiss, Germany) in “Nanotech” ISPMS SB RAS.

3. Experimental results and discussion

3.1. Electrical conductivity

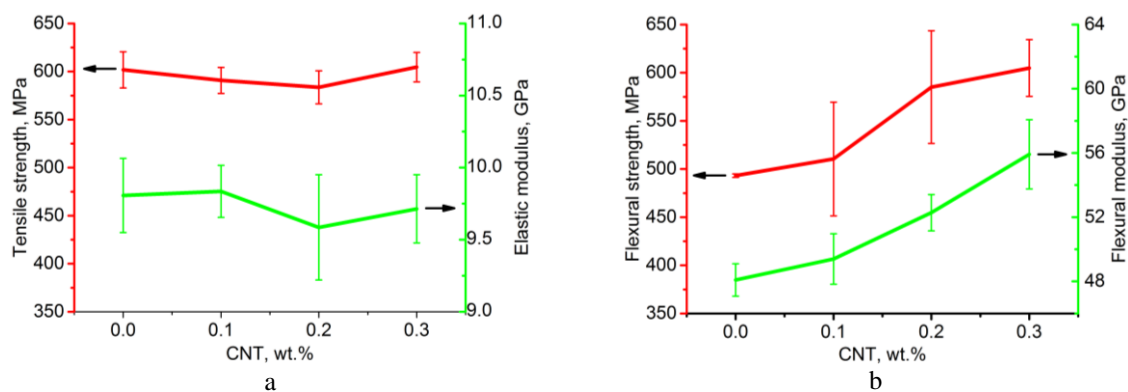
The results of conductivity measurement are presented in Table 1. The in-plane conductivity of CFRP depends only on the surface fiber layer thus in-plane conductivity demonstrates the slight increase with the addition of CNTs however the CNT-0 specimen is conductive as well: 564 S/m. Quite identical results of out-of-plane through-thickness and diagonal measurements along with null conductivity for CNT-0 are showing that the final electrical conductivity of hybrid CFRP in out-of-plane mode is dictated by epoxy matrix. Thus the addition of CNTs enhances conductivity in final hybrid CFRP even if it was zero at the initial state without fillers. Table 1 shows the electrical properties for modified and non-modified specimens measured in three directions.

Table 1. Electrical conductivity of specimens.

Specimen	Electrical conductivity, S/m		
	CFRP in-plane surface	CFRP out-of-plane diagonal	CFRP out-of-plane through-thickness
CNT-0	564±319	<10 ⁻⁵	<10 ⁻⁵
CNT-1	514±252	6.8±1.5	7±1.18
CNT-2	702±228	16.1±1.5	16.3±1.02
CNT-3	865±184	65.3±11.1	66.2±9.9

3.2. Tensile and flexural testing

Three specimens were tested for each content of CNTs. The failure mode at the tension of all specimens was a lateral crack at the grip. Figure 2a demonstrates the plots of mean ultimate strength and modulus. It can be seen from the results in figure 2a that ultimate tensile strength and modulus are not significantly affected by addition of CNTs. The result is agreed with theoretical assumptions: tensile strength and modulus depend mainly on the longitude oriented fibers while the impact of a binder is small.

**Figure 2.** Ultimate tensile strength and modulus (a) and flexural strength and modulus (b).

In flexural tests the strength and stiffness of the matrix greatly influence the final properties of CFRP/SWCNT hybrid composites. The shearing stresses occurring in interlayers of a bended specimen are born by the binder. Thus modification of matrix should improve flexural mechanical properties.

Figure 2b presents the results of a 3-point bending test. It can be seen that both flexural strength and modulus were increased by 23% and 16% correspondingly for the specimen with the addition of 0.3 wt.% of SWCNT. Such a modification increases the flexural strength of hybrid composite, but the scatter is quite high for CNT-1 and CNT-2. Flexural modulus with increase of CNTs demonstrates a uniform growth with the average scatter. The increase of flexural properties is attributed to higher shear strength of binder and adhesion between the layers after modification.

3.3. Scanning electron microscopy

Figures 3 and 4 show SEM images of initial structure and fractured epoxy specimens CNT-0 and CNT-3 respectively. The (a) images demonstrate the polished edge of the CFRP specimen while (b) and (c) are fractography images captured after flexural testing.

The figure 3a evidences the lack of conductivity resulting in the formation of the overexposed areas while for the specimen CNT-3 the image of the CFRP structure is quite uniform (figure 4a). As can be seen, both specimens have good uniformity of structure with no pores and damages.

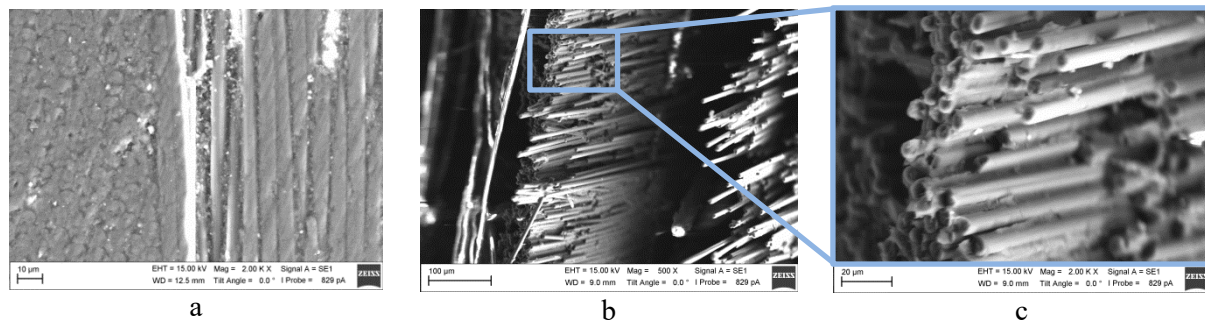


Figure 3. SEM images of CNT-0 specimen: initial structure (a) and fracture surface (b).

By comparison of fractography results of specimens CNT-0 and CNT-3 we can conclude that the fracture of these specimens occurs differently. Due to the increase of the elastic modulus and reduced viscoplastic properties of the modified binder, there form a lot of small crushed fragments between the filaments during testing of CNT-3 (figure 4c) while the non-modified epoxy binder remains good plasticity (figure 3c).

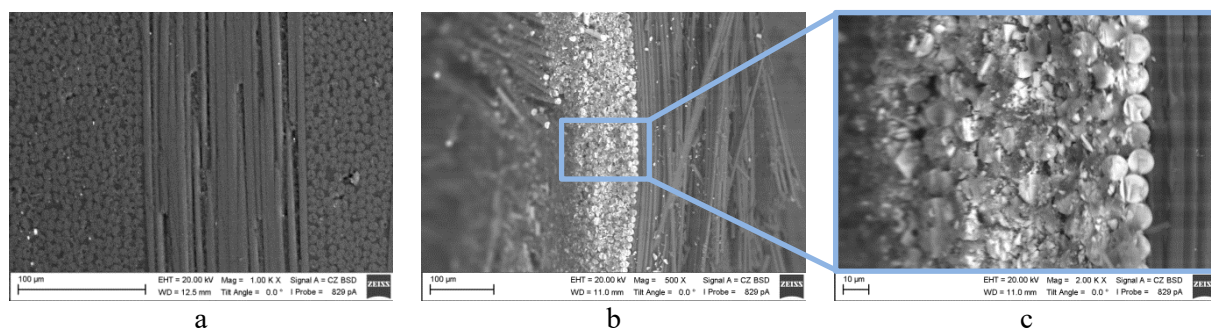


Figure 4. SEM images of CNT-3 specimen: initial structure (a) and fracture surface (b).

4. Conclusion

The hybrid CFRP/SWCNT composites were investigated. The research was focused on the evaluation of electrical and mechanical properties. It has been shown that tensile properties are less affected by the addition of SWCNT while flexural were improved. Flexural strength and modulus increase after the addition of 0.3 wt.% of SWCNTs by 22% and 16% correspondingly. Electrical conductivity after the addition of SWCNT increased as well. The effect of SWCNTs on CFRP conductivity is much higher for the out-of-plane path provided by interlayer connections in epoxy binder while in-plane conductivity determined by carbon fibers and therefore it shows an ambiguous increase with large scatter. The addition of 0.3 wt.% of SWCNT leads to increases of out-of-plane conductivity up to ~66 S/m while unmodified CFRP was dielectric. The method proposed in the work for producing hybrid composites has good potential and future research is to be linked to the development of reliable and inexpensive preparation and mixing technique and investigation of fatigue properties which are quite important for industrial application.

Acknowledgements

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