Increase of composite structures strength by carbon fiber surface modification with spray deposited carbon nanotubes

D D Levin¹, A V Romashkin¹, Yu A Polikarpov¹, N S Struchkov¹, A V Kireynov² and I A Komarov²

¹ National Research University of Electronic Technology, Moscow, Russian Federation
² Bauman Moscow State Technical University, Moscow, Russian Federation

Abstract
The possibility of carbon fiber and the polymer matrix interfacial interface improvement by modification carbon fiber surface with functionalized carbon nanotubes. Nanotubes were deposited to carbon fiber surface by aerosol spray deposition, to increase the tensile strength of composite structures. The relationship between the tensile strength of the composite structure with the epoxy matrix and the uniformity of carbon nanotube coating was investigated.

Keywords: CARBON FIBER, EPOXY MATRIX, CARBON NANOTUBE, COMPOSITE STRUCTURE, INTERFACIAL INTERFACE, TENSILE STRENGTH

1. Introduction
Improvement strength properties of new composite materials requires increasing its strength properties without deteriorating other parameters of the structure as a whole, and without substantially increasing the cost of production. Carbon nanotubes (CNTs), due to their mechanical, thermal and electrical properties, are considered as promising materials for modification of the polymer matrix or filler of polymer composites [1]. The main problem in nanoscale fillers containing materials production is the uniform distribution of the filler in the polymer matrix of the composite. In particular, distribution of the CNTs in the composite is often implemented by ultrasonic processing [2, 3]. In order to improve the interaction of CNT with polymer matrix CNT surface is often functionalized by amino- or carboxyl groups. However, it is not always possible to realize the optimal interaction between the filler and the matrix, which can lead to the absence of a noticeable effect of improving the characteristics [4]. The large surface area of CNTs, together with their outstanding physical and mechanical properties is probably the main reason of significant improvement of the nanocomposite mechanical properties due to interaction of CNTs with polymer macromolecules. However, to reach such improvement in the properties of the CNT modified composite, it is necessary to find an optimal way to improve CNTs interaction with the polymer matrix on the one hand and with carbon fiber at the same time. Carbon fiber plays the role of a cheaper filler material that provides sufficient strength of the composite at the micro and macro levels. The result of modification is an increase of the strength characteristics of composite material, that was the purpose of this work.

2. Materials and methods for tasks resolving, accepted assumptions

This work is licensed under the Creative Commons Attribution 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by/3.0/ or send a letter to Creative Commons, PO Box 1866, Mountain View, CA 94042, USA.
In order to investigate the effect of CNT addition to the carbon fiber surface on the tensile strength of a composite material, a series of experiments was carried out. Three types of the samples of carbon fiber/epoxy composite were manufactured and tested. Different samples containing: uncoated fibers (reference sample), carbon fiber coated with CNT (type 1), carbon fiber coated with CNT and tetraethylenetetramine (TETA) (type 2). Carbon fibers (Toho Tenax, Tenax-E HTS45 E23, linear density 800 tex, Japan) with a thread diameter of about 5.5 mkm were used as the basis for the composite material. The sample was a bundle of carbon fibers with dimensions of 5x150 mm. Carbon nanotube layer was applied to the carbon fiber surface by iterative spray-deposition with small flow of the dispersion per unit of time (no more than 0.2 ml/min, at a pressure in the compressed air line of about 2 atm, on the substrate heated to 75ºС during deposition). To prepare the dispersion of CNT in N-methylpyrrolidone (NMP) and a mixture of solvents (NMP and cyclohexanone (CG)) with concentration of 62 μg/ml, carboxylated CNTs (P3-SWNT, Carbon Solutions Inc., USA) were used [5]. The solution of tetraethylenetetramine (TETA, Dow Chemical, the Netherlands) with a concentration of 12 μg/ml in a mixture of isopropyl and benzyl alcohol was used for modification of previously deposited CNT to obtain the second type of samples. The TETA solution was deposited using a method similar to that used for the deposition of CNTs, and the amount of the deposited solution was also the same and did not depend on the number of deposited CNTs. Unmodified epoxy resin with medium viscous based on bisphenol-A (Araldite LY-556, Huntsman Inc., USA) was used as the matrix. It was prepared for “hot” curing together with the hardener isomethyl tetrahydrophthalic anhydride (isom-MTHPA, Chimex Limited, China) which amount was 90% by weight based on the weight of epoxy resin used, to which an additional 2-methylimidazole (0.2 weight % from epoxy resin weight) is added, which is a curing accelerator agent in the composition of the hardeners "hot" curing mixture. The glass transition temperature of the binder was about 140 ºC. Samples were made by the wet impregnation method. Carbon fibers were soaked in a bath with a binder. Than the samples were cured on the holder, providing the tension of the samples, that was strips of fibrous material that were soaked of the binder. The curing mode was 4 hours at 110 ºC. Lining pads for gripping specimens in tensile testing machine was made of basalt plastics.

The tensile strength was measured on a Zwick Z 100 tensile testing machine at a loading rate of 10 mm/min. Distance between clamping jaws was 60 mm. The tests were carried out in accordance with ASTM D 2343-09. During the tests, the load, the modulus of elasticity and the elongation at break were determined by stretching the specimen with the help of a testing machine until the specimen failed. During the test, a stress-strain diagram was recorded.

3. Results

It was found that using a mixture of solvents NMP and CG allows to obtain uniformly distributed CNTs on the carbon fiber surface (Fig. 1a) while the deposition of CNTs from the solution of pure NMP leads to the formation of conglomerates (Fig. 1b).
An important aspect of the formation of a composite structure with increased strength characteristics is the preliminary processing of the initial carbon fiber [6]. This effect presumably was reached by presence of carboxyl- (type 1 samples) and amino groups (type 2 samples) on the surface of CNTs. Static tensile strength measurements for samples with a cross section of 0.44 mm$^2$ for all specimens types showed the following results of the average values for the Young's modulus, ultimate strength, ultimate elongation respectively: 167.8 GPa, 3355.3 MPa, 0.97 mm (reference samples, averaging over 5 samples); 164.5 GPa, 2352.0 MPa, 0.65 mm (type 1 samples, averaging over 2 samples); 157.0 GPa, 3947.0 MPa, 1.38 mm (type 2 samples, averaging over 3 samples); and 166.5 GPa, 3815.0 MPa, 1.18 mm (type 2 samples with a 2-fold increase in the amount of CNTs, averaging over 2 samples).

4. Discussion of the obtained results and comparing with previously known works

Based on a comparison of the CNTs distribution uniformity on fibers surface the following conclusions were made. The CNTs distribution uniformity on the carbon fiber surface significantly affects the nature of the interfacial interaction of the polymer matrix with carbon fiber. Modification of the surface with CNTS leads to an increase in the 14-18% ultimate strength, as well as 20-40% in the ultimate elongation of the sample, and without a significant change in the modulus of elasticity as opposed to samples without modification of carbon fibers. This result correlates with previously known results on increasing the strength of composite materials containing carbon nanomaterials, where the introduction of nanoparticles in the whole volume was carried out however, with increase in the strength of the composite by more than 2 times [7]. At the same time, even a small amount of carbon nanotubes (twice reduced for simply type 2 samples) applied to the surface has a significant effect on the ultimate tensile strength and maximum elongation increment. But the average value of the elastic modulus in this case was slightly reduced relative to reference samples. This decrease can be explained by the excessive amount of TETA molecules applied on top of the CNT in the case of a smaller amount of CNTs for the 2nd specimens type, that led to greater ultimate deformation before rupture and the maximum possible elongation in combination with the minimum elastic modulus. The average number of CNT fibers distributed over the carbon fiber surface was up to 1% of the area in the case of the deposition of CNT from a dispersion with NMP and CG, while deposition from pure NMP gave up to 5% filling of the surface area of carbon fiber. Taking into account the obtained data on tensile strength measurement, excessive addition of CNT (type 1 samples) between the carbon fibers in combination with the lack of necessary functional groups (amino groups in this case) for effective binding with the epoxy matrix.
leads to a significant decrease in ultimate strength and elongation at break. However, the modulus of elasticity is on the same level with unmodified carbon fibers. In addition, the formation of CNT conglomerates during depositing from a dispersion with pure NMP associated with insufficient temperature of carbon fibers upon the process of CNT deposition. As a result, agglomeration of microdroplets as they are sprayed leads to uneven deposition of CNTs as microdroplets dry out and can also cause a decrease in tensile strength [8, 9]. The addition of a solvent with a low boiling point leads to a decrease in the size of the droplets and promote an increase in the residual solvent evaporation rate, contributing to a more uniform coating of carbon fibers.

5. Conclusion
The surface of carbon fibers can be uniformly covered with a CNT mesh by the iterative spray-coating that leads to reinforcement of final composite materials. The surface containing CNT mesh can be also modified with TETA molecules and these processes leads to increase in tensile strength of 14-18% and maximum elongation of 20-40% while maintaining the elasticity modulus at the level of values characteristic of unmodified samples. At the same time, it is necessary to maintain an optimal ratio between the amount of CNT and TETA deposited to carbon fiber surface, as well as the uniformity of the distribution of CNTs, the role of which appears to be quite significant when filling up to 1% of the surface area. This last fact makes it possible to implement a low-cost modification of carbon fibers with the formation of new generation composite materials with improved characteristics.

Acknowledgments
This work was supported by the Ministry of Science and Higher Education of the Russian Federation, Agreement No. 14.574.21.0184 (unique ID RFMEFI57417X0184)

References
[1] Thostenson E T, Chou T W 2006 Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. Carbon 44 № 14 P. 3022-3029.
[2] Heimann M et al. 2008 Investigations of carbon nanotubes epoxy composites for electronics packaging. Electronic Components and Technology Conference 2008. ECTC 2008. 58th. – IEEE, – P. 1731-1736.
[3] Bauhofer W, Kovacs J Z 2009 A review and analysis of electrical percolation in carbon nanotube polymer composites. Composites Science and Technology. 69 № 10 P. 1486-1498.
[4] Loos M R et al. 2008 Effect of carbon nanotubes addition on the mechanical and thermal properties of epoxy matrices. Materials Research. 11 № 3 P. 347-352.
[5] Itkis M E et al. 2003 Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solution-phase near-IR spectroscopy. Nano Letters. 3 № 3 P. 309-314.
[6] Dai Z et al. 2011 Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion. Applied Surface Science. 257 № 20 P. 8457-8461.
[7] Guo H et al. 2014 Preparation and mechanical properties of epoxy/diamond nanocomposites. Polymer Composites. 35 № 11 P. 2144-2149.
[8] Singh B P et al. 2015 Solvent free, efficient, industrially viable, fast dispersion process based amine modified MWCNT reinforced epoxy composites of superior mechanical properties. Adv Mater Lett. 6 № 2 P. 104-113.
[9] Nelyub V A et.al. 2016 Capillary Hydrodynamics of Oligomer Binders. Polymer Science, Series D, 9 № 3 P. 322–325