Increasing the resistance to interlayer shear of composite materials due to the modification of carbon fabric fibers with carbon nanotubes

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Abstract. Interlaminar shear strength is an important characteristic of the characteristics of composite structures. This article presents the results of an experimental study of the role of carbon nanotube reinforcement of a fibrous filler of carbon fabrics in increasing the interlayer shear strength of composite articles made of carbon fiber reinforced plastics. Studies were conducted using dry roving carbon twill weave (Twill type grade: 3K, 2 x 2 Twill Weave Carbon Fiber Fabric, 5.7 Oz / Sq Yd, 50 “Wide, .012” Thick, and 3K, 2 x 2 Twill Weave). The creation of carbon composite materials based on a polyester matrix with additional reinforcement using grown carbon nanotubes (CNTs) on filler fibers has been proposed and investigated. It is shown that with a uniform distribution of CNTs on filler fibers, the interlayer shear resistance increases by 60%.

Key words: nanodispersions, nanocomposite, carbon nanotubes (CNTs), polyester resins, hybrid nanocomposite.

1. Introduction.

Polymer composite materials are widely used in various industries, including aircraft and rocketry [1-7]. They ensured a reduction in the mass of load-bearing structures due to their low density, high strength and rigidity. In particular, Airbas has successfully used carbon fiber in aircraft wings. Composite missile bodies are highly resistant to environmental influences.

Carbon ribbons and fabrics of various types, which are composed of parallel or interlaced fibers, are produced on an industrial scale and can be used in composite fabrication processes after impregnation.

At the same time, polymer composites can solve larger technical problems if a number of constraints are overcome. First of all, it is low interlaminar shear strength. There are well-known approaches to eliminating these disadvantages, such as changing the microrelief of the fiber surface and reducing structural defects in materials [8], improving the adhesion between the fibers and the composite matrix [9-14], including the impregnation of fibers with dressings [15]. A very important approach to improving the characteristics of composites is to develop special methods for additional interlayer reinforcement of composites [16-19] and metallization of fibers [20-22] by vacuum arc or magnetron sputtering [23]. In particular, the metallization of the fibers provides an increase in the resistance to interlayer shear by 20 ... 30%.

At the same time, the reinforcement of the matrix, including nanomodification [18, 19], does not significantly affect the strength characteristics of power composite materials. This can be explained by the insufficient interaction of the reinforcing elements of the material structure with the filler fibers. So nanoparticles do not get into the interfiber space during the impregnation of the strands, being filtered at the boundaries. In order to drastically increase the resistance to interlayer shear, in this work, nanotubes were grown on fibers before their subsequent impregnation with a binder.
2. **Synthesis of carbon nanotubes on reinforcement fibers**

CNTs were grown on dry twill roving carbon fabric (Twill type: 3K, 2 x 2 Twill Weave Carbon Fiber Fabric, 5.7 Oz / Sq Yd, 50 "Wide, .012" Thick, as well as 3K, 2 x 2 Twill Weave) (Fig. 1, A).

The growth of CNTs on carbon fibers was carried out using the gas pyrolysis method (CVD - process). The fabric was impregnated with a catalyst solution and heated in a reactor at a temperature of 6500 °C and atmospheric pressure to fix the catalyst on the surface of the fibers. To carry out the process, the reactor was filled with hydrogen (H2) for 2 minutes to fix the catalyst, and then propane was filled with a butane mixture to ensure the growth of CNTs. To control the CNT length, the gas consumption was reduced so that the growth of the CNT length decreased from a maximum speed of 2 μm s⁻¹ to ~ 0.3 μm s⁻¹, and during the growth of 0.5–5 min, the length was 10–100 μm.

![Figure 1. Scanning electron microscope (SEM) images of carbon fabric used in laminate production: A - without CNTs; B - with CNTs grown on the fiber surface, as well as individual fibers coated with CNTs. Resolution on the bottom images A and B ~ 20 μm](image)

The length of CNTs, as a rule, is much greater than the distance between the layers of the fabric (~ 10 μm) and between the fibers in a strand (~ 1 ÷ 5 μm). The CNTs grown on the fibers were examined using a scanning electron microscope (SEM). The difference between fibers before and after CNT deposition can be observed by comparing Fig. 1A and 1B. The study of SEM images showed that the distribution of CNTs on the outer surfaces was uniform, with the exception of the extreme rows of tissue, where the tissue is damaged. Therefore, in the manufacture of laminate samples, the damaged areas were removed.

The CNT diameter and the uniformity of their distribution were estimated using a transmission electron microscope (TEM). It was found that CNTs grew uniformly and densely in the radial direction on the surface of each individual fiber in the tissue (Figure 1B, bottom). Analysis of multilayer TEM - photo showed that CNTs grown on fibers have an outer diameter of ~ 17 ± 2 nm and 8 concentric layers.

As a result of impregnation with polyester resin, a new structure is obtained - a hybrid composite, where nanoadditives are present not only in the polymer matrix, but also on the fibers. In the literature, such a composite is called free reinforced plastic (FFRP).

A study of the wettability of CNTs with a thermosetting polyester resin showed that CNTs are easily impregnated with such polymers by the capillary method [25], and that the adhesion between CNTs and thermosetting plastic creates a strong composite. Thus, due to the synthesis of CNTs directly on the fibers
and their uniform distribution, additional reinforcement of the composite material occurs, increasing its strength.

3. Preparation of Hybrid Composite Specimens for Testing Interlaminar Shear Resistance

To assess the effect of CNTs on the interlayer shear resistance, two groups of samples with and without CNTs were prepared using the following technology. Square cards were cut from carbon fabric and stacked on top of each other in 12 layers. Half of the obtained multilayer workpieces were grown with CNTs on fibers, and the other half remained unchanged. The weight of the obtained samples was measured.

A propane – butane mixture, which filled the volume between the fibers of the fabric, was used as a carbon source for growing CNTs. The number of CNTs in the bulk of the samples remained approximately unchanged. But the length of CNTs was obtained equal to ~ 10 μm, ~ 40 μm, and ~ 100 μm by varying the duration of the CVD process, which corresponded to approximately 0.6%, 2%, and 3% of the CNT content in the composite. This was done to analyze the effect of the CNT length on the interlayer shear resistance. It is characteristic that with an increase in the CNT length, tissue swelling and a slight increase in the thickness of the laminated workpiece were observed.

The resulting laminated preforms were placed in a vacuum bag and subjected to vacuum infusion impregnation. Then the impregnated workpiece in a vacuum bag was placed in a metal mold, the surface of which was laid with a non-perforated Teflon film. The samples were prepared for 9-12 h under a pressure of ~ 200 KPa at room temperature (~ 25 °C).

When analyzing the prepared samples, the proportion of resin was determined by subtracting the mass of the fabric and CNTs from the total mass of the composite.

The volumes of the fractions were calculated taking into account the density of the resin, and the total density of the binder together with CNTs was considered equal to ~ 1.4 mg / mm³ [26]. The mass fraction of CNTs was found to be ~ 0.5–2.5%, and the volume fraction of CNTs ranged from 1% to 3%. The volume fraction of fibers in the hybrid and base composite is ~ 60%, and the resin is ~ 40%. The possible influence of the error in the dosage of the catalyst mass and the error in the dosage of CNTs were not considered, considering these errors to be insignificant.

A scanning electron microscope was used to study the morphology of the initial samples and hybrid composites. The images in the optical and scanning electron microscope demonstrate the presence of CNTs over the entire cross section of the laminated sample, and the absence of differences between samples with and without CNTs (Fig. 2).

The resin, when impregnated under vacuum, completely impregnated all fibers together with CNTs. Cross-sections of samples without CNTs (Figure 2C) and with CNTs (Figure 2D) demonstrate excellent bonding and resin impregnation of hybrid layers. The distance between the fibers in the hybrid composite is slightly larger than in the base sample due to the separation of the fibers by growing CNTs, as mentioned above. The dark circles at the edges of the hybrid composite fibers (Figure 2D) are explained by the fact that the SEM charge creates dark halos at the interface between the individual fibers and the conductive matrix with CNTs. It was not possible to examine individual CNTs inside hybrid laminated samples.

Rectangular specimens (Figure 3D) were sawed off with an abrasive wheel, and the ends were sequentially hand-sanded with 1200, 2400 and 4000 grit sandpaper to relieve stress concentrators. Samples length ~ 100mm, width ~ 10mm. Change in length and width within ± 2%. The average thickness of one layer in the original composite (~ 0.6 mm) is slightly less than that of the hybrid composite (~ 0.7 mm), which reflects an increase in tissue volume due to the mutual repulsion of fibers from each other, due to the growth of CNTs. To assess the mass and volume fractions, each piece of tissue was weighed using a balance (accuracy - 1μg) before and after the introduction of CNTs. It was assumed that the measured weight of the CNT fabric and the weight of the catalyst fabric did not change during the curing of the resin. The practical yield of CNTs per 1 g of fabric is 0.3 g.
Figure 2. Image of hybrid composite samples with 0.2% CNTs:

A: 3-layer sample after trimming; B: SEM pattern of intersecting fabric layers of the impregnated sample; C: SEM cross-sectional pattern of composites without CNTs; D: SEM picture of the cross section of composites with CNTs.

4. Results of testing samples for resistance to interlayer shear

The determination of the interlaminar shear strength was carried out on a Zwick Z100 testing machine, which provides deformation at a constant rate of 1 mm/min and measurement of the load with an error of no more than 1%. The testing machine (fig. 3) is equipped with a tip and supports allowing the distance between the supports to be adjusted.

Figure 3. Photo of the testing machine and the sample when determining the interlaminar shear strength

Tests were carried out on 12-layer laminates under continuous loading of specimens until failure. In our experiments, the distance between the supports is assumed to be 1 = 30mm. The sensors of the testing machine automatically recorded the load at the moment of sample delamination in the region of its ends (Fig. 4). The tests for each condition were repeated 5 times.
Figure 4. The appearance of the separation of the samples at their ends after testing

The apparent ultimate strength at interlaminar shear in accordance with the standard [24] was determined by the formula:

$$\tau = 0.75 \frac{F}{S},$$

where $F$ is the load force at the moment of delamination of the ends of the sample, $S$ is the cross-sectional area of the sample.

As follows from Table 1, the laminated sample from the hybrid composite showed characteristics 60% higher than the sample without CNTs.

Table 1. Results of comparison of breaking shear strength for laminated samples made of composite without CNTs and with CNTs

| Properties                      | Sample without CNT | Sample with CNT | Difference |
|---------------------------------|--------------------|-----------------|------------|
| Resistance to interlayer shear, MPa | 18.2±1.0          | 30.0±1.0        | +60%       |

5. Conclusions.

1. Creation and research of hybrid nanocomposites showed that the application of the method of gas-phase growth of carbon nanotubes ensures their uniform distribution on filler fibers, and impregnation with a binder reliably bonds the nanotubes to the fibers.

2. The shear strength of hybrid nanocomposites based on a polyester matrix increased by 60%. An increase in other strength characteristics can also be expected.

3. Additional studies are required to determine the optimal characteristics of CNTs in the complex structure of hybrid nanocomposites, including length, diameter, mass fraction.

4. Additional research is needed to clarify the optimal parameters of hybrid nanocomposites with other fillers and binders.

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