

Synergistic effect of the strength increasing of fiberglass by reinforcing epoxy binder with carbon nanotubes



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Introduction: Fiber reinforced polymer composites, due to the outstanding mechanical properties and low density have been extensively used in high performance applications, such as aerospace, automotive, shipbuilding and sports. The using of the nanosized particles as a fillers of polymer binder in order to improve the physical and mechanical characteristics of polymer composites is relevant and actively investigated in recent years.



Multi-walled carbon nanotubes and their oxygen-modified forms

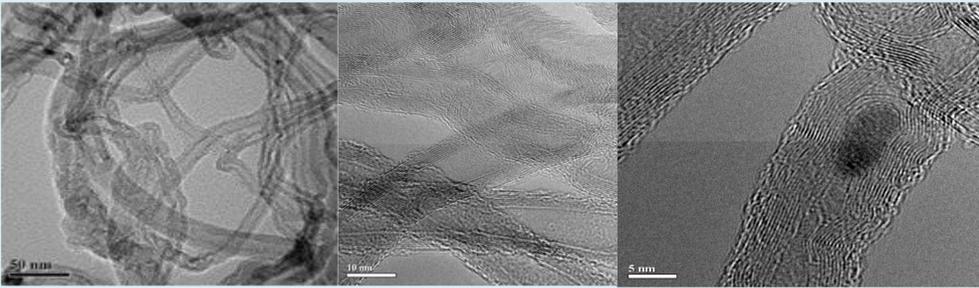
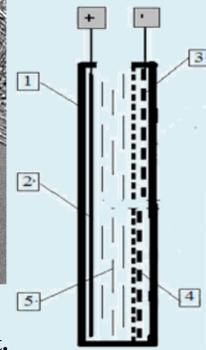


Fig. 1. TEM images of carbon nanotubes

CNT: Young's modulus ~1.8 TPa; Tensile strength ~150 GPa; Aspect ration $\eta \geq 10^3$; $F_c \approx 1/\eta \sim 0.1\%$ wt.



Modification of CNTs by oxygen under controlled conditions of anodic oxidation in concentrated sulfuric acid

Fig. 2. Scheme of vertical electrochemical reactor: 1-body, 2-anode, 3-cathode, 4-separator (membrane), 5 - CNTs

Samples of CNT's	Table 1. Relative concentration of oxygen-containing groups, %			
	$E_b = 286.1-286.3$ eV (C-OH)	$E_b = 287.3-287.6$ eV (C=O)	$E_b = 288.4-288.9$ eV (C-OOH)	$E_b = 290.4-290.8$ eV (CO, CO ₂)
Initial	49.1	17.2	17.2	16.5
120 A·h/kg	53.8	19.8	13.6	12.8

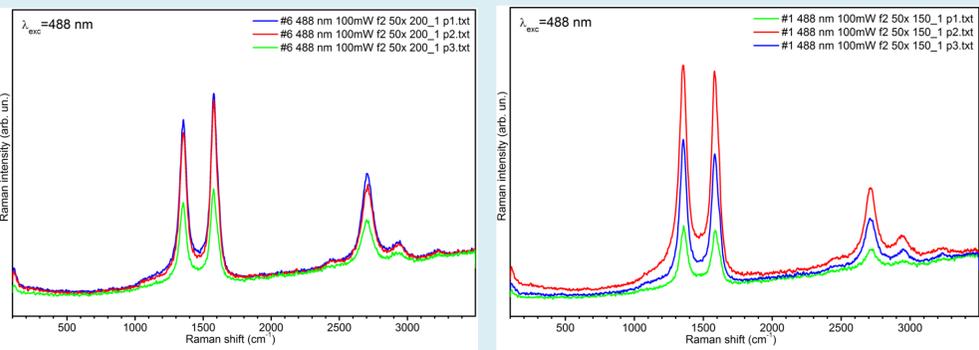


Fig.3. Raman spectra of CNTs: Initial – left, after transmission of 120 Ah/kg – right

Table 2. The basic parameters of the characteristic bands, which are manifested in the micro-Raman spectra of CNT's of different degrees of oxidation

Samples CNT's	D, cm ⁻¹	G, cm ⁻¹	2D, cm ⁻¹	D _{FWHM} , cm ⁻¹	G _{FWHM} , cm ⁻¹	I _D , a.u.	I _G , a.u.	I _D /I _G
120 A·h/kg	1352	1583	2711	55	59	11.78	11.34	1.04
initial	1348	1573	2706	51	53	9.0	10.4	0.86

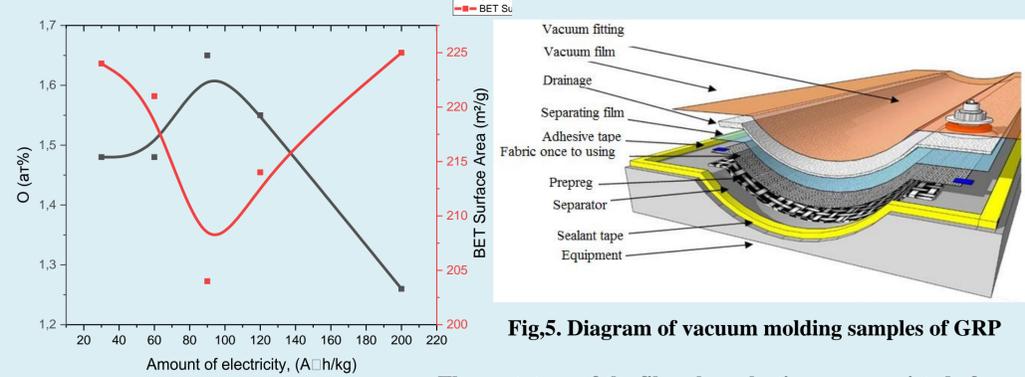


Fig. 4. Dependence of oxygen content from O1s XPS spectra of and specific surface area determined by nitrogen adsorption-desorption on the amount of electricity passed

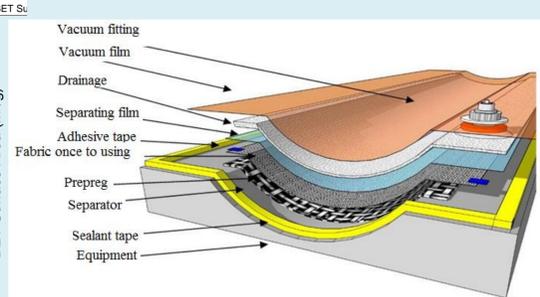


Fig.5. Diagram of vacuum molding samples of GRP

The prototype of the fiberglass plastics were consisted of two layers of fiberglass with a density of 110 g/m² with a core of PVC foam bonded with a binder: an epoxy resin LR 285 with a polymerization catalyst LH286 filled with CNTs or their modified oxygen or nitrogen forms. CNTs were injected into the epoxy resin on a three-roll mixer, and the polymerization catalyst - by ultrasonic treatment. Model specimens were obtained by vacuum pressing. The scheme is shown in Fig. 5.

Mechanical characteristics of composite materials

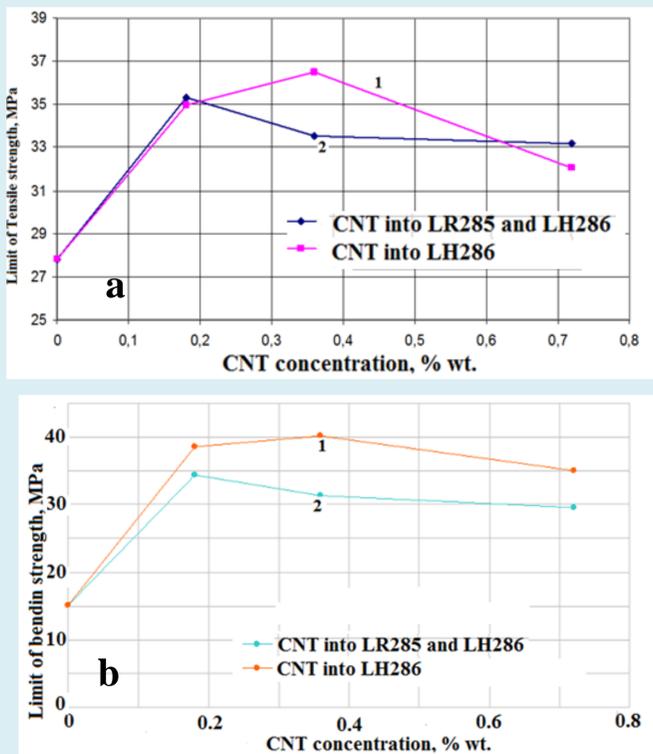


Fig. 6 – The limit of tensile strength (a) and bending strength (b) of the layered composites & CNT content

№ example	Component of the composition	The content of CNTs, %		The total content of CNTs in terms of solid resin, %	Tensile strength, MPa	Changing the tensile strength, %
		non-oxidized, hydrophobic	oxidized			
1	Epoxy resin	0	0,25	0,25	46,0	70
	Hardener	0,25	0			
2	Epoxy resin	0	0,1	0,15	40,0	48
	Hardener	0,3	0			
3	Epoxy resin	0	0,1	0,5	51	89
	Hardener	1,5	0			
4	Epoxy resin	0	1,0	1,0	56	107
	Затверджувач	1,0	0			
5	Epoxy resin	0	2,5	1,9	39,0	44
	Hardener	0,3	0			
6	Epoxy resin	0	2,5	2,2	28,5	5,6
	Hardener	1,5	0			
7	Epoxy resin	0	0	0	27,0	—
	Hardener	0	0			

Conclusion. Reinforcement of epoxy resin brand LR 285 by mixing with oxidized CNTs on the mixer with three rolls for two-layer sample of fiberglass increases the its tensile strength by 59%, and the initial CNTs by ultrasound in amine hardener LH 286 - by 54%. If, at the same time, oxidized CNTs and initial CNTs are reinforced into resin and the hardener in the same amount as in first time, a synergistic effect is observed: the strength limit is almost doubled. This effect is explained by the fact that the amine hardener in the interaction with CNTs acts as a surfactant. In this case, it orients the hydrocarbon part to the CNTs, and the amino groups - outwards, which confirms our quantum chemical calculations [1]. The resulting surface layer prevents reverse agglomeration of CNTs after dispersion. Because, it is the amino groups that react with the epoxy groups of the resin, the interaction of the polymer matrix with the surface of the CNT is enhanced. For oxidized CNTs, the opposite is true. In the case of dispersion of oxidized CNTs in the resin, the most oxygen-containing groups on the surface of CNTs (due to their polarity) prevent reverse agglomeration after dispersion.

Cherniuk O.A., Demianenko E.M., Terets M.I. et al. Study of the mechanism of influence of carbon nanotubes surface chemistry on the mechanical properties of fiberglass // Appl Nanosci.-2020.-10.P. 4797–4807.