MATERIALS SCIENCE

UDC 546.01 **Complex Use of Mineral Resources. № 4. 2016.**

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CARBON NANOPARTICLES INFLUENCE on MECHANIC PROPERTIES of EPOXIDE RESIN and CARBON COMPOSITE. REVIEW

Abstract: Increasing breaking strength of epoxide resin (ER) and carbon composite is an aim up-to-date for many machinery sections: space, aviation, defense, automotive, and others. The aim is achieved via numerous methods of ER and carbon composite modification. ER modification is carried through injection of various chemical compounds. One of efficient modification method assumes introduction of carbon nanoparticles (CNP): carbon nanotubes (CNT), fullerenes, astralenes, graphenes. CNP's feature is formation of aggregates in polymers, therefore their disintegration is a complicated, yet necessary procedure. The article contains experimental data of CNP influence on breaking strength of ER available in literature. The authors analyzed methods of CHP dispersion in ER. Sensitivity coefficients K_σ and K_E were introduced to explain strengthening features of CNP, they reflect percentage change of breaking strength limits and material elasticity module under condition of introducing 1 % by CNP mass to ER or carbon composite. Sensitivity coefficients for ER: CNT are K_σ =18-600, K_E = 5-153; fullerenes – K_σ = 1,2 -424, K_E =168; astralenes – K_σ = 666; graphenes – K_σ = 80-909. The optimal quantities of CNP introduction to ER are 0.05-0.3 % and it depends on completeness of dispersion of nanoparticles, further increase of CNP introduction leads to decrease in breaking strength. Greater spread of sensitivity coefficients should be mainly attributed to completeness of CNP dispersion in ER samples, and to the lesser extend – to peculiarities of CNP from different production batches. Upper values of coefficient are important for practice, since they reflect availability of the technology. CNT length almost does not have any impact on the strengthening effect. Availability of carbon nanotubes makes them most promising hardeners for industry technology of carbon composites. The paper discloses efficiency of applying functionalization (preliminary chemical treatment) of CNP. Functionalization of CNP facilitates increasing of K_σ ratio by 14-48 %. Liquids with amino-groups create greatest impact on CNP among other functionalization agents. Also the paper covers carbon plastic. CNT strengthen carbon plastic with coefficient K_σ = 1-399, K_E =9-635, fullerenes – K_σ = 37, astralenes – K_σ =14-24, K_E =6. In the case of CNT result is equal to ER data. The acquired data is necessary to elaborate domestic technology for production of super-strong and high-module carbon plastics.

Key words: carbon nanoparticles, modification, functionalization, dispersion, epoxide resin, carbon plastic, strengthening.

Introduction. Construction materials primarily are characterized by breaking strength limits and elasticity module, which may vary greatly for every given material. Strength features of metal alloys are improved by highly complex alloying procedures, thermal treatment, degasifying, deformation, nanostructuring [1-3], and composite materials (composites) – by improving matrix and carcass characteristics, increasing connection stability, outgassing, optimizing space location of carcass [4-7]. Materials with moderate and average strength features are normally available in free international market. Highly strong are both expensive and sometimes unavailable, because many of them are included in lists of goods and technologies of dual, rocket, nuclear designation set out by international agreements for export control. So, for instance, export control applies to highly strong materials and technologies of their production: aluminum alloys with strength limits ≥ 415 MPa, magnesium alloys with ≥ 345 MPa, titanium alloys with ≥ 900 MPa, matensite aging steels with ≥ 2000 MPa, carbon plastics with ≥ 415 MPa [8].

According to Table 1 highest readings of marginal limit strength is displayed by beryllium alloys, fiber glass plastic and carbon plastic. Beryllium is a rare metal, its production is limited, technology of extraction and application are ecologically hazardous [9, 10]. These are the main reasons why beryllium and its alloys are used only in special cases. Fiberglass reinforced plastic is available, yet, it has a low level of elasticity module, therefore, it greatly deforms under loads. In general, carbon plastic is available, it has high elasticity module, which makes it most demanded super strong material usable for strong elements in machinery and construction. It is more and more widely used in aviation, rocket technologies, space apparatus building, automotive industry, sports equipment, everyday goods.

Table 1 – Features of some most strong brands of construction materials [8]

Material	Compression breaking strength, MPa	Density, kg/m^3	Marginal compression strength, kN • m/kg	Average (normal) elasticity module, M • m/kg
Epoxy resin	50-170	1250	40- 136	28
Manganese alloys	150- 400	1800	83- 222	90
Aluminum alloys	150- 700	2800	54-250	250
Steels	500- 3000	7800	64- 385	260
Titanium alloys	450-1400	4500	100-311	245
Beryllium alloys	400-1520	2200	182-690	1160
Fiber-glass plastic	35-1100	1,8	19-611	220
Carbon plastic	100-1100	1,58	63- 700	1160

Main (matrix of) carbon plastic is epoxy resin (ER), at the same time it is of independent interest as construction, electric insulation material, glue. Epoxy resin strengthening is an actual task as well.

Driven by work undertaken in Kazakhstan and aimed at establishing an industry for production of aerospace, defense, automotive machinery becomes a need of creating superstrong carbon plastic becomes more demanding. Competitive carbon plastics for aerospace feature strength of ≥ 525 MPa (for comparison – 2 industrial samples of carbon plastic by different producers bought in market, demonstrated strength limits of 110 and 115 MPa). Such a material can be created only using entire arsenal of strengthening methods. One of first techniques for strengthening ER and carbon plastic is modifying them by injecting carbon nanoparticles (CNP) [11]. Detailed analysis of available publications must precede experimental research of the method applicability.

Goal of the Paper is analysis of literature data to modify (strengthen) ER and carbon plastic by introducing different types of CNP to identify most efficient modification ways to achieve most desirable effect.

Carbon nanoparticles (CNP) and methods to functionalize them. In 1991 Japanese scientist Iijima generated carbon nanotubes. Normally nanotubes are one to ten nanometer in diameter and several micrometers long. Nanotubes can be both single-layer and multilayer – inserted one into another [12].

Another achievement of nanotechnology is discovery of fullerene, which is one of allotropic modification of carbon. First, fullerenes C_{60} and C_{70} were synthesized in 1985 by H. Kroto and R. Smalley from graphite put under influence of powerful laser beam [13]. It became possible to generate C_{60}-fullerene in quantities sufficient for research in 1990, it was acquired by D. Huffman and W. Kretchmer, who performed evaporation of graphite with electric arc in helium environment [14]. Fullerene molecules may hold from 20 to 540 carbon atoms placed at the top of polygon surface, shaped as reduced icosahedron. Every carbon atom in C_{60} molecule is located at top of two hexagons and one pentagon, and in principal it cannot be distinguished from other carbon atoms. Carbon atoms creating the sphere are interconnected by strong covalent forces. Thickness of the sphere shell is 0,1 nm, C_{60} molecule radius is 0,357 nm. Length of the C-C bonding in the pentagon is 0,143 nm, and 0,139 nm in the hexagon.

Astralenes belong to fullerene compound, they represent polyhedral structures made of carbon atoms is the size of 80-150 nm. Polygons consist of major defect-free flat graphite surface laid from 20-50 graphene sheets, interconnected by defect edge areas of the pentagon structures. Astralenes come as byproduct of fullerene production, as thermal dispersement of graphite anode in plasma of arch charge, burning in an atmosphere of inactive gas [15].

Graphene is two-dimensional form of carbon, it is a one-atom thick film, crystal carcass of which is shaped as hexagonal net. One of the methods for graphene extraction is based on mechanical cleavage and pealing graphite layers from high-profile pyrolytic graphite [16].

CNP feature high surface energy (chemical free valence), which creates certain problems for their dispersement in epoxy resin. On one side CNP come into reaction with epoxy resin creating heat, from the other side – the particles create strong aggregates (agglomerates) that are hundreds mkm in size, this hinders aggregation of stable dispersement in water and organic environments, including polymers. Discharging or elimination of surface CNP energy is possible by way of covalent addition of functional groups or non-covalent retention of chemical compounds by the surface particles: oxidation, treating by acids and other liquids. Destruction of CNP aggregations in a liquid and their dispersement is carried by ultrasound treatment [11,17- 23].

CNP oxidation is one of the most wide-spread modification methods. Most often used agents for oxidation are oxygen-containing acids and mixtures

based on them: HNO_3, HNO_3+ H_2SO_4 with mass ratio of 3:1, $HClO_4$, H_2SO_4, HNO_3 + $K_2Cr_2O_7$, H_2SO_4+$KMnO_4$, H_2SO_4+H_2O_2, compounds containing amines. Normally acid treatment is a multi-hour (up to 24 hours) process, executed in boiling agent mass. After such functionalization, hydroxyl, lactone and carboxyl and amines can be identified at the particle surface. Oxidation system containing hydrochloric acid, hydrogen peroxide, potassium permanganate, persulfates, hypochlorides and others as main components can be effective. Long-term treatment of CNP by Fenton agent (mixture of hydrogen and iron susphade (II)) generates hydroxyl groups on the surface. Possibly, CNP oxidation by plasma at atmosphere pressure by carbon dioxide, water vapor, air oxygen, ozone, vapors of nitric acid [18].

Analysis of CNP dipersement in epoxy resin. As said before, CNP, when introduced to a liquid, form firm aggregates of size equal to hundreds of mkm. In the case, their strengthening function in a polymer shall be weak. In this view, aggregates introduced to ER must be destructed and dispersed to the level of base nanoparticles. The better CNP dispersement process is carried, the higher is the ER strengthening effect. In the works [24-26] they used a method of CNP dispersement to epoxy resin, consisting of the following steps:

1. CNP is put into a vessel with ethanol and then is dispersed by submerged ultrasound treatment. Ethanol is a source of hydroxyl groups giving functionalizing effect, and ultrasound destructs CNP aggregates;

2. Epoxy resin is introduced to the gel and the mixture is stirred by ultrasound for 1-2 hrs;

3. Ethanol is evaporated from the epoxy resin in a vacuum stove over 6-48 hours at 80°C. Functionalized and dispersed CNP is left in epoxy resin;

4. High-temperature hardener is added to epoxy resin, the mixture is stirred till homogeneous spread in magnetic of mechanic stirrer at 2000 rev/min or ultrasound during 15-60 min.;

5. Strengthening of the epoxy composite is carried in vacuum stove at room temperature at 140°C for 8 hours or for 7 days.

In the work [27] CNP dispersement was carried by the scheme set out above, however, the authors used methanol instead of ethanol. In the works [28, 29-31] acetone or acetone with surfactants was used instead of ethanol. Nonylphenolethoxylate, polyoxitelen 8 lauryl, potassium dodecilsuphate were used as surfactants [29-31]. In works [32-34] before dispersement CNP were preliminarily treated by HNO_3 и H_2SO_4. In works [35, 36] significant improvement of CNP dispersement through their preliminary functionalization by acid and further flourating.

As one can see, the described CNP dispersement into ER are complex enough, therefore they should be completed in full to achieve efficient application of potential opportunities provided by CNP.

Influence of carbon nanoparticles on mechanical properties of epoxy resin. Table 2 summarizes test data of work with CNP: CNP, fullerenes, astralenes, graphenes. We have deducted the following sensitivity ratios to characterize CNP influence on ER strength:

- tensile strength or compression strength limit to CNP:

$$K = \frac{\Delta\sigma}{\sigma_0 \Delta n} 100\% \qquad (1)$$

- elasticity module for tensile or compression strength to CNP:

$$K = \frac{\Delta E}{E_0 \Delta n} 100\% \qquad (2)$$

where $\Delta\sigma = \sigma_{max} - \sigma_0$, where σ_0 – initial reading of strength limit, σ_{max} – maximum strength limit; $\Delta E = E_{max} - E_0$, where E_0 – initial elasticity module, E_{max} – maximum elasticity module; $\Delta n = n_{max} - n_0$, where n_0 – initial CNP content, n_{max} – CNP content at maximum strength limit or elasticity module. CNP parameters: *D* – internal diameter, *d* – external diameter, *l* – length.

Physical meaning of the deducted ratios K_σ and K_E means percent variation of strength parameters σ and E at conditional introduction into ER or carbon plastic of 1 % of CNP mass. These coefficients aid carrying comparative analysis of various test data.

Table 2 data demonstrates the following regularities. Introducing CNP into ER leads to increasing strength limit and elasticity module. Dependence of strength limit and elasticity module of ER on percent of introduced CNP consists of growth, maximum and decrease sections. No published sourced have so far clearly explained this phenomenon.

The greatest number of works is dedicated to CNP, most likely because among other CNP this material is most available. Let us focus on these particles. K_σ ratio of strengthening happened to be much larger during compression testing 600 % and 230 % (subitem 1.2.1 and 1.2.2) of multilayer CNP, if compared to test data for tensile strength from -3 % to 153 % (subitem 1.1, 1.1.1, 1.2.3, 1.2.4). This difference illustrates that ER is a kind of material most efficiently operating when compressed. Please note the following test data of subitems 1.2.1 and 1.2.2: in the first case initial strength or ER of

Table 2 – Influence of non-modified CNP on ER

№	CNP	Epoxy resin / hardener	% input	s		E, ГПа		K_σ or $K_{E,}$ %	Notes	Source
				comp.	tens.	comp.	tens.			
1	CARBON NANOTUBES									
1.1	1 layer	(DGBEA (L137i/ H137i	0		63,8		2,6	18 26*	D < 2 nm, l – several mkm	[37]
			0,05		65,84		2,6			
			0,1		66,34		2,6			
			0,3		67,28		2,8			
1.1.1		Epon 862/ Epon W	0		83,0		2,0	-3 5*	D - 1-1,4 nm, l = 0,1-1 mkm	[38]
			1		79,8		2,1			
			0,1		-		2,7			
			0,5		-		2,7			
1.2	Multilayer									
1.2.1		DER-330/ PEPA	0	55		2,0		600 70*	D -10-30 nm, l - 1-4 mkm	[39]
			0,05	70		2,2				
			0,1	88		2,4				
			0,3	87,5		2,6				
			0,5	72		2,7				
1.2.2		ED-20/ iso-MTGFA	0	130				230		[40]
			0,05	145						
			0,1	138						
			0,2	135						
			0,3	134						
			0,4	132						
			0,5	129						
1.2.3		Epon 862)/ Epikure W	0				1,9	39*	l- 1-1,5 mkm	[41]
			0,1				1,6			
			1,0				2,4			
			2,0				3,4			
1.2.4		Bisfenol A/ scented hardener	0				1,3	153*		[42]
			0,5				1,7		l- 50 mkm	
			0,5				2,3		l-10 mkm	
			0,5				2,1		l - 1 mkm	
			0				1,3	100*		
			1				2,3		l- 50 mkm	
			1				2,6		l-10 mkm	
			1				2,4		l - 1 mkm	
			0				1,3	29*		
			4				2,6		l- 50 mkm	
			4				2,8		l-10 mkm	
			4				2,8		l - 1 mkm	
2	FULLERENES									
2.1.		Araldite / DEH24	0	110		4,92		424 168*	C_{60}, purity 99,9 %	[43]
			0,02	118		5,11				
			0,04	122		5,22				
			0,06	138		5,45				
			0,08	145		5,70				
			0,10	163		5,83				
			0,12	166		5,91				
2.2			0		85		2,8	1,2		[44]
			1		86		3,1			
2.2			2		87		3,0	11*	$C_{60,}$ D - 0,75 nm	[44]
			3		87		2,9			
3	ASTRALENES									
3.1		D.E.N. 431/ DADFS	0		52,6			7832	D - 40-60 nm	[45]
			0,005		73,2					
			0,01		49,8					
			0,05		46,9					

DER-330/ PEPA make equals to 55 MPa, this stated, sensitivity ratio K_σ equals to 600 %, in the second case with make ED-20/iso-MTGFA initial strength equals to 130 MPa and K_σ =230 %. Resin ED-20 with iso-MTGFA hardener is peculiar because of its viscosity. Resin DER-330 with PEPA hardener, on the opposite, is moderately strong, high flow and ability to moisten. Thus, it is possible to conclude the following: the higher the resin flow, the higher is the effect of CNP strengthening. Test data regarding influence of nanotube length on ER strengthening effect (subitem.1.2.4) is of interest, results are given on Figure. These data illustrates that length of nanotubes influences strengthening effect almost no-how.

In case of fullerenes (item 2) the CNP regularities are the same in general. The greatest value of the ratio K_σ = 424% was acquired during compression tests, tensile tests yielded K_σ=1,2. Moving to review of findings generated from astralene testing. It is possible to assume that abnormally high value of K_σ=7832% for sample tensile strength testing (item 3.1.) resulted from a test mistake for the case of CNP contest 0,005%, when hardness value equaled to 73,2 MPa. If this test peak is ignored, the strengthening values confirm regularities derived in cases of CNP and fullerenes: sample compression tests K_σ =600 %. Graphene compression tests yielded K_σ = 909 %, tensile testing K_σ = 80 %.

Overall, limits of changes to sensitivity ratios of ER to CNP were as follows: for CNP – K_σ =18-600 %, K_E = 5-153 %; fullerenes – K_σ = 1,2–424 %, K_E = 168 %; astralenes – K_σ = 666 %; graphenes – K_σ = 80-909 %. Maximum ER hardness values are achieved through 0,05-0,3 % CNP introduction. Abnormal spread of sensitivity ratios draws special attention, we believe simple spread of test data does not explain this. Most likely, some physical and chemical process is behind this, the process not considered at the stage of test setting. It is worthwhile to assume that such process is the process of CNP dispersement into ER, the degree of completeness of which was not controlled by the authors hereto. In the test works, low values of

sensitivity ratios K_σ and K_E yielded at low degree of CNP agents dispersement to initial nanoparticles, and other way round. The given data speaks of a need to introduce new control parameter of the process CNP dispersement into a polymer – dispersement ratio. This issue requires separate review.

In practice, highest values of sensitivity ratios of K_σ and K_E are of special interest in terms of production of superstrong ER and carbon plastic, since they reflect achievability of the material strengthening technology when applying the method. Thus, potential of strengthening ER with various CNP types were: for CNP – K_σ = 600 %, K_E = 153 %; fullerenes – K_σ = 424 %, K_E =168 %; astralenes – K_σ = 666 %; graphenes – K_σ = 909 %. It is just to state that the efficiency of the reviewed CNP types proved to be the same.

It is worth mentioning that practical application of fullerenes, astralenes and graphenes is restrained by absence of industrial scale production. High power requirements of production underlay final product costs. I.e., NeoTechProduct LLS (Saint-Petersburg) price 10 grams of ash with 7 % content of fullerenes at almost 425 KZT, 1 g of C_{60} fullerenes (99,9 % purity) amounts to 9000 KZT, 1 g of C_{70} fullerenes (99 % purity) – 31300 KZT [48]. Cost of carbon nanotubes is times less, making it possible to use them in various industrial technologies.

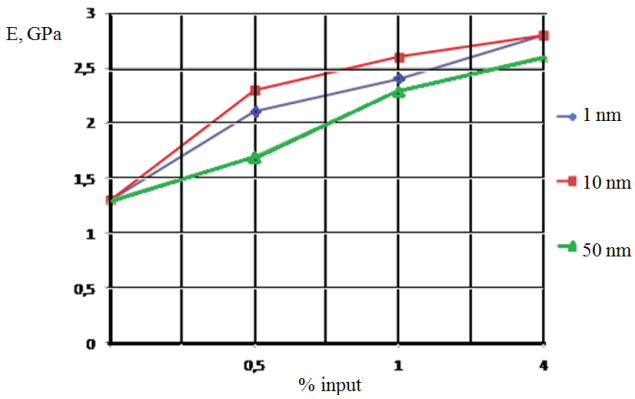

Figure – Influence of CNP length on elasticity module [42]

All of the issues reviewed above concerned CNP without any additional treatment. Meanwhile, work aimed at improving features of CNP surfaces by way of additional treatment with different liquids has started, such treatment is called functionalization. We shall review possible influence of CNP functionalization on ER strength. Work [49] studied influence of single layer carbon nanotubes (OCNP) functionalized by NH_2 amines on mechanical properties of epoxy resin. ER was injected with the same amounts of 1 % initial and functionalized CNP, growth of strength limit and elasticity module for tensile strength was 30 %. In the work [50] functionalizing double layer and multilayer carbon nanotubes with amines under the condition of the same injection of 0.5 % yielded 10 % strength growth. The authors of works [51] achieved 24 % growth of tensile strength at 0,5 % injection into ER of CNP functionalized by amines. Work [52] carried covalent functionalization of 1 % CNP; tensile strength growth amounted to 14 %. Work [53] carried comparative influencing on strength properties of CNP functionalized by carboxyl and hydroxyl groups. At 0.25 % CNP content in ER, tensile strength growth for carboxyl groups gave 6 %, Jung module – 3 %, for hydroxyl groups these properties were equal to 1 % and 4 %. Work [54] functionalized surfaces of multilayer CNP by carboxyl groups (COOH), injection of 1 % of such particles yielded compression strength growth of 24 %. Another work [55] stated that non-covalent functionalization of 1 % (poly 4-aminostyrene) yields tensile strength growth of 34 %, Jung module – by 40 %. This results state that CNP functionalization results in K_σ ratio growth of range from 14 to 48 %. Therefore, CNP functionalization procedure proved its efficiency, and it should be recommended as part to the technology of production of superstrong carbon plastic.

The given findings drive to the following conclusions:

– Injecting CNP to ER can yield a 60-90 % growth of strength limit.

– Dependency of ER strength limit on CNP injected consists of sections of growth, apex and decrease. Apex of ER strength limit falls at 0,05-0,3 % of CNP injected.

– Different CNP may yield the following sensitivity ratios for the strength growth section: for CNP – K_σ =600 %, K_E = 153 %; fullerenes – K_σ = 424 %, K_E =168 %; astralenes – K_σ = 666 %; graphenes – K_σ = 909 %. These parameters are reached under the condition of high level of CNP aggregates dispersement into ER down to initial nanoparticles.

– CNP length has almost no effect on its capacity to strengthen ER.

– CNP functionalization can increase K_σ ratio by 14- 48 %.

– Among other CNP, carbon nanotubes are most promising for applied technologies, they are produced on industrial scale and are affordable.

Modifying carbon plastic by carbon nanoparticles. Carbon plastic consists of epoxy resin matrix and carbon carcass. In general ER strength is lower than the strength of carbon carcass (fiber,

roving), considering this, the stronger the epoxy component of the compound is, the stronger the material is in general. The acquired regularities of ER strengthening by injecting CNP can be translated to carbon plastic by properties.

There are little works dedicated to strengthening carbon plastic by injecting CNP. Background search identified several works relating to the topic reviewed, finding are summarized in Table 3.

Table 3 – CNP influence on carbon plastic strength

№	CNP % input	σ, MPa		E, GPa		K_σ or K_E, %				Source
		comp.	tens.	comp.	tens.					
1	CARBON NANOTUBES									
1.1 Single layer										
1.1.1	0	488				1				[56]
	5	501								
	10	539								
1.1.2	0	552			53,8	399		635		[57]
	0,05	662			70,9					
1.2 Multilayer										
1.2.1	0	370				84				[58]
	0,2	487								
	0,5	514								
	1	681								
1.2.2	0	506	371	73,2	63,22	7	14	28	25	[59]
	2	650	518	114	104,6					
	3	603	522	112	109,8					
	5	675	499	73,6	66.5					
1.2.3	0	602				33				[58]
	0,2	593								
	0,5	776								
	1	802								
1.2.4	0				32,1	9				[60]
	0,5				30,3					
	1				32,9	9				[60]
	1,5				36,5					
2	FULLERENES									
2.1.1	0	830				37				[61]
	1	1140								
3	ASTRALENES									
3.1.1	0	573	560		110	14	24	6		[62]
	3	820	90		130					

CNP influence on the strength of carbon plastic is strongly mediated by various carcass types, bonding of carcass and matrix, compound production peculiarities. Table 3 data shows, that in general, sensitivity ratio of carbon plastic relating to CNP is lower than the same ratios for ER properties. However, some carbon plastic samples (item 1.1.2) have same K_σ values, tending to the ratio values of carbon plastics. This result is of principal matter, since it defines the level of potential achievability of the result. We have not succeeded finding any works published on the topic of researching the matter of CNP functionalization influence on strength properties of carbon plastic. Nonetheless, it can be expected that CNP functionalization can yield an effect comparable to the one of ER.

The task of producing super-strong carbon plastic requires full cycle of the above mentioned method of ER strengthening by introducing CNP. Matters of CNP influence on the strength of ER bond with carbon matrix, on other technological processes of carbon plastic production. Best possible method of applying CNP as carbon plastic hardener requires running extra tests.

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ТҮЙІНДЕМЕ

Эпоксидті шайыр (ЭШ) мен көмірпластиктің беріктігін жоғарылату технологиясын жасау мәселесі техниканың көптеген салалары (ғарыш, авиация, қорғаныс, автокөлік, т.б.) үшін өзекті болып табылады. Бұл мәселені ЭШ-ді және көмірпластик компонентерін модификациялау амалдарымен шешуге болады. ЭШ-ді әртүрлі химиялық қосылыстарды енгізу арқылы модификациялауға болады. Модификациялаудың ұтымды тәсілдерінің бірі – көміртекті нанобөлшектерді (КНБ) (көміртекті нанотүтіктерді (КНТ), фуллерендерді, астралендерді, графендерді) енгізу болып табылады. КНБ-тер үшін полимерлердегі агрегаттардың қалыптасуы тән болады, сондықтан олардың диспергиялануы өте маңызды және күрделі мәселе болып табылады. Жұмыста КНБ түрлерінің ЭШ-дың беріктігіне әсер етуі бойынша әдебиеттердегі эксперименталды мәліметтер жинақталған. КНБ-нің ЭШ-ға диспергиялану әдістеріне талдау жасалынған. КНБ-нің беріктікті жоғарылату мүмкіндіктерін сипаттау үшін сезімталдық коэффициенттер $К_σ$ және $К_E$ енгізілген. Олар ЭШ-ға немесе көмірпластикке салмағы бойынша 1 % КНБ-ді шартты түрде енгізгенде беріктік шегінің және серпімділік модулінің пайздық өзгеруін көрсетеді. ЭШ үшін сезімталдық коэффициенттер келесідей шықты: КНБ үшін – $К_σ$ =18-600, $К_E$ = 5-153; фуллерендер үшін – $К_σ$ = 1,2 -424, $К_E$ =168; астралендер үшін – $К_σ$ = 666; графендер үшін – $К_σ$ = 80-909. ЭШ-ға КНБ-ді енгізудің оңтайлы шамасы 0,05-0,3 % құрайды және нанобөлшектердің диспергиялану толықтығына байланысты болады. КНБ-ді енгізуді ары қарай ұлғайту материалдың беріктігін төмендетеді. Сезімталдық коэффициенттерінің әртүрлі болуын көбіне ЭШ-ғы КНБ диспергиялануының толықтығымен, сонымен қатар КНБ әртүрлі жасау партияларының ерекшеліктерімен байланыстыру керек. Тәжірибе үшін коэффициенттердің жоғарғы шектері маңызды, өйткені олар технологияның қол жетімділігін көрсетеді. Нанотүтіктердің ұзындығы беріктікті нығайтуға әсер етпейді деп айтуға болады. Нанотүтіктердің қол жетімділігі оларды көмірпластиктердің өнеркәсіптік технологиялары үшін беріктікті жоғарылатудың ең перспективті қоспалар ретінде қарастыруға мүмкіндік береді. КНБ-ді функционалдауы (реактивтермен алдын ала өңдеу) тиімділігі қарастырылған. КНБ-ді функционалдау $К_σ$ коэффициентін 14-48 %-ға жоғарылатуға мүмкіндік береді. Қарастырылған КНБ-ді функционалдағыштардың арасында аминтоптары барларының тиімділігі ең жоғары болған. Жұмыстың екінші бөлігі көмірпластикке арналған. Бұл жағдай үшін эксперименталдық мәліметтер ЭШ үшін қарағанда аздау болды. КНБ көмірпластиктің беріктігін келесі коэффициенттермен жоғарылатады: $К_σ$ = 1-399, $К_E$ =9-635; фуллерендер – $К_σ$ = 37; астралендер - $К_σ$ =14-24, $К_E$ =6. КНБ үшін нәтижелер ЭШ үшін алынған мәліметтермен бір шамада болды. Алынған мәліметтер беріктігі жоғары және жоғарымодульды көмірпластикті жасаудың отандық технологиясын әзірлеу үшін қажетті.

Түйінді сөздер: көміртекті нанобөлшектер, модификациялау, функционалдау, диспергиялау, эпоксидті шайыр, көмірпластик, беріктікті жоғарылату.

РЕЗЮМЕ

Задача создания технологии упрочнения эпоксидной смолы (ЭС) и углепластика актуальна для многих разделов техники: космической, авиационной, оборонной, автомобильной и др. Вопрос решается многочисленными приемами модификации ЭС, компонентов углепластика. Модификация ЭС осуществляется путем ввода различных химических соединений. Одним из эффективных способов модификации является введение углеродных наночастиц (УНЧ): углеродных нанотрубок (УНТ), фуллеренов, астраленов, графенов. Для УНЧ характерно образование агрегатов в полимерах, ввиду этого, их диспергирование является не простой, но важной задачей. В работе собраны имеющиеся в литературе экспериментальные данные по влиянию различных видов УНЧ на прочность ЭС. Проанализированы методы диспергирования УНЧ в ЭС. Для характеристики упрочняющих возможностей УНЧ введены коэффициенты чувствительности $К_σ$ и $К_E$, которые отражают процентное изменение предела прочности и модуля упругости материала при условном вводе в ЭС или углепластик 1 % по массе УНЧ. Коэффициенты чувствительности для ЭС получились для: УНТ равными $К_σ$ =18-600, $К_E$ = 5-153; фуллеренов – $К_σ$ = 1,2 -424, $К_E$ =168; астраленов – $К_σ$ = 666; графенов – $К_σ$ = 80-909. Оптимальный ввод УНЧ в ЭС составляет 0,05-0,3 % и зависит от полноты диспергирования наночастиц, дальнейшее увеличение ввода УНЧ приводит к снижению прочности материала. Большие разбросы коэффициентов чувствительности стоит связывать, главным образом с полнотой диспергирования УНЧ в образцах ЭС, в меньшей степени – с особенностями УНЧ различных партий изготовления. Для практики важны верхние значения коэффициентов, поскольку они отражают достижимость технологии. Длина нанотрубок практически не влияет на эффект упрочнения. Доступность углеродных нанотрубок делает их наиболее перспективными упрочнителями для промышленных технологий углепластиков. Рассмотрена эффективность применения функционализации (предварительной обработки реактивами) УНЧ. Функционализация УНЧ позволяет увеличить коэффициент $К_σ$ на 14-48 %. Наибольший эффект из расмотренных функционализаторов УНЧ дают жидкости содержащие аминогруппы. Также в данной работе рассмотрены углепластики. УНТ упрочняют углепластик с коэффициентами $К_σ$ = 1-399, $К_E$ =9-635; фуллерены – $К_σ$ = 37; астралены - $К_σ$ =14-24, $К_E$ =6. Для случая УНТ результат оказался одного порядка с данными по ЭС. Полученные данные необходимы для разработки отечественной технологии производства высокопрочных и высокомодульных углепластиков.

Ключевые слова: углеродные наночастицы, модификация, функционализация, диспергирование, эпоксидная смола, углепластик, упрочнение.

Received 10.08.2016.