Filling with the Graphene Nanoplates as a Way to Improve Properties of Epoxy-Composites for Industrial and Geophysical Machinery

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Abstract: It is established that the filling with graphenes increases (by 1.3-1.8 times) the strength at normal adhesion to steel. At same time, filling reduces the compressive strength and abrasion resistance and also resistance to aggressive liquids (conc. nitric acid, chloromethylene; mixture acetone-ethylacetate). The most probable reason for this may be the features of the graphene plate structure, prone to deactivation (self-rotation) of particles and therefore sensitive to the technology of hardening. Studies have shown the limited positive effects of graphene as a filler of epoxydes, although its introduction can significantly improve certain practical characteristics (adhesion, thermal and electrical conductivity).

Keywords: Epoxy-Resin, Graphene, Compressive Strength, Bending, Adhesion, Swelling, Thermograms

1. Introduction

Graphene is a new type of carbon materials, that forms 2D-structures. Structurally graphenes are monoatomic folias from sp²-hybridized atoms of C, packed in two-dimension cell structures with distance of C - C even 0,142 nm. He has very high electro- and thermo-conductivity. Therefore, the specific structure of graphene can result in creation of electroconducted composites and substantial his strengthening, in particular strengthening of adhesion to the metallic surfaces.

Theoretical predictions of their existence have been made for a long time. But as the graphene material was discovered only in the last decade - by A. Geim and V. Novosëlov (ex-soviet physicists who received the Nobel Preemie for this) [1]. Immediately, its unusual properties were discovered [2-17], after which a boom in the research of graphene-polymer and other systems began.

The introduction of graphene into polyepoxide leads (according to our data) to the formation of beautiful glossy coatings (figure 1). This allows you to count on graphene as an additive for simple (without complex technologies and

temperatures) manufacturing of aesthetic plastic cases, parts, thermal bonding glues for appliances and machines. High interest in such coatings and compounds is shown by manufacturers of mobile communication and geological equipment, as well as large-scale engineering

2. Methods & Reactives

2.1. Preparation and Structure of Graphene

Obtaining of lamellar plates (FLG-plates, figure 1) of graphenes from graphite flakes was carried according to the method of solubilisation, improved by Shulga-Ogenko [2]. The scales were filtered, washed first with a distillate, and then three times with ethanol, and dried. Then they were dispersed in boiling ethanol (8 g/l) and processed with 20 kHz ultrasound until a stable suspension (in which they are stored permanently) is formed.

2.2. Preparation of Composites

Alcoholic solutions (based on the dispersion of graphite in

alcohol) of the 2015 g series with specific weights of 8 and 31 g/l were used.

The epoxy resin Epoxy-520 (Czech prod., EU) was mixed with an alcohol solution of graphene in proportions of 0.01 to 5 wt% from EtOH-solutions. The curing was carried out with

the polyamine PEPA (resin: PEPA = 7:1) after 2 weeks of preparation. Cured composites were poured into molds or smeared with a thin layer on the bonded surfaces. After 5 days, they (except swelling samples) were treated at 75°C for 3 hours.

Figure 1. SEM-image of our graphene.

2.3. Strength Tests

The tests on compression and tensile (flexural) strength, and tests on tearing adhesion to steel were used (figure 2). The templates-cylinders $d=8\text{mm}$, $h=12\text{ mm}$ were compressed. For tensile (flexural) strength, templates-plates $60\times10\times2\text{ mm}$ were tested. For adhesion, steel cylinders (5 cm^2) were glued and teared. Abrasion were measured as mass-loss at wear by P60-paper (wear way is $60\times20\text{ cm}$).

Figure 2. Visualisation of test methods.

3. Result and Discussion

3.1. IR-Spectroscopy and Microscopy

From the IR spectra it is seen that after 2 wt% -filling the intensity of signals increases (only the peaks of the original oligomer are weakened at $1880\text{--}2089\text{ cm}^{-1}$, Figure 2), although their number and location are practically not changes. Considering that the signals for 1040 , 1083 , 1250 cm^{-1} and others (see table 1) are the most characteristic for a cured epoxy resin, it is possible to assume deeper polymerization

after filling.

According identification of Dobrotvor\Starokadomsky [18-19], IR of cured composites show the change (intensification) of the intensities of the bands after filling (Figure 2). Thus, in the unfilled band, 573 cm^{-1} is clearly visible, according to [19, 20] (see Table 1) characteristic of the uncured epoxy oligomer. But in spectra of epoxy-graphene, it is replaced by a strong 560 cm^{-1} - signal of the polymer (see table 1). Similarly, the signal of the uncured in the unfilled at 1043 cm^{-1} is inferior to the polymer signal at 1043 cm^{-1} (Figure 3). Also, in filled the signal - at 833 cm^{-1} (for polymer) is much stronger.

Figure 3. IR-reflection spectra for unfilled (bottom) and filled with 2 wt% of graphene (upper).

The signals of the epoxy groups (844, 1260, 1362 and 1384 cm^{-1} etc.) do not appear in all the spectra, i.e. curing can be considered very complete (for epoxydes it is near 95%). At the same time, the presence of distinct bands at 574 and 1888 cm^{-1} , and especially epoxy groups at 2068 cm^{-1} (and

also weak signals in the region of 2100-2812 cm^{-1}) suggests that even in composites there is an appreciable fraction of uncured resin, who decreases with filling (Table 1). All this can speak of a better curing of a filled composite than an unfilled one.

Table 1. Characteristic of some IR signals of the epoxy ED20-hardener's system.

Signal according [19] (and our analogue), cm^{-1}	Identification [19-20]
554 (560)	Epoxy-polymer, valent. CH_2 -
574 (573)	Initial epoxy-olygomer, valent. $-\text{CH}_2$ -
828 (833)	Polymer, pendulum oscillation $-\text{NH}-$
1036 (-)	Polymer, benzol rings and valent wobbles of CN -groups.
1044 (1043)	Initial epoxy-olygomer, benzol rings
1180 (1184)	Polymer, amino-groups
1254 (1254)	Polymer, $\text{OH}-$ or amino-groups
1260 (-)	Initial epoxy-olygomer, epoxy CO -groups
1310 (1310)	Polymer, $\text{OH}-$ or amino-groups
1462 (1457)	Polymer, benzol rings
1510 (1514)	Polymer, amino-groups
1608 (1608)	Polymer, primary amino-groups
1610 (-)	Hardener PEPA, valent. $-\text{CH}_3\text{C}- + -\text{C}-\text{C}-$
1890 (1888)	Initial epoxy-olygomer, valent $-\text{CH}-$
2068 (2068)	Initial epoxy-olygomer, valent. epoxy-groups
2968 (2964)	Polymer, valent. $-\text{CH}_2-$, $-\text{CH}-$, $-\text{OH}-$, $-\text{CH}_3\text{C}-$

Figure 4. Micro-images of compositions before hardening (length of image E is 1)1,75; 2) 0,7; 3) 0,35 and 4) 0,175 mm).

According to the microscopy (Figure 4), the composition contains comparatively large aggregates of graphenes, the dimensions of which can reach 0.4 mm (Figure 4). In composition are stabilized rare microbubbles of air, coated with a relatively thick graphene film (up to 0.02 mm, Figure 4C).

3.2. Strength and Resistance Tests

Our experiments allowed to set very considerable

strengthening influence of graphene on epoxycomposite adhesion to steel surface (table 2). This influence increases with the height of grapheme concentration. At small concentrations of graphene (for example the 0,05 wt%) influence on adhesion is insignificant (table 2). A microscopy shows aggregative morphology of compositions (figure 4) with the presence of graphene particles to $d \approx 0,4$ mm and including of phials of air.

Table 2. Strength of the adhesion tearing of steel cylinders ($S = 5 \text{ cm}^2$) glued by composites with 0.01 - 5 wt% of graphene (31 and 8 g/L).

Graphene, 31 g/L in ethanol solution	Unfilled (0%)	0.05 wt%	2 wt%	5 wt%
Load of tearing Q, kgf	70	65	190	240
% to Q for unfilled	100%	93%	271%	343%
8 g/L in ethanol solution	Unfilled (0%)	1 wt%	2 wt%	5 wt%
% to Q for unfilled	100%	112%	175%	130%

But filling with graphene do not increases any strength properties. The flexural (tensile) strength after low-filling varies little (and at 0.1 wt% the modulus rises), but decreases with comparatively large ones (Table 3). The compressive strength (Table 4) slightly increases only in the region of 0.01% by weight, in other cases it decreases.

Table 3. Flexural (tensile) strength for templates with 0, 0.05 – 2 wt% of graphene.

	Strength, σ kgf/cm	Modulus, $\times 10^3$ kgf/cm ²
Unfilled	7,2	19
0.01 wt%	7,2	19
0.05 wt%	7,2	17
0,1 wt%	-	21
0,5 wt%	-	17
1 wt%	-	16
2 wt%	5,7	-

Table 4. Strength at compression of templates with 0.01 – 5 mac% of graphene.

Graphene, 31 g/L in ethanol solution	H (0%)	0.01 wt%	0.1 wt%	0.5 wt%	1 wt%
Loading, kgf	410	435	390	370	340
% to Loading for unfilled	100%	106%	95%	90%	83%
8 g/L in ethanol solution	H (0%)	1 wt%	2 wt%	5 wt%	
% to Loading for unfilled	100%	88%	96%	93%	

Table 5. Other fixed characteristics of composites.

	H (0%)	0,05wt%	2wt%	5wt%
Time for destruction in conc. HNO ₃ , days	8	7	2	1
Time for destruction in acetone: ethylacetate, days	≥ 100	≥ 100	≤ 1	≤ 1
Shrinkage, mm for h=12 mm	2	1,5	0,01	0
Abrasion, mg	85	75 (better than H)	90 ($\approx$ to H)	118 (worse than H)

The introduction of graphene allows shrinkage shrinkage, and at relatively high percent shrinkage disappears altogether (Table 5). Resistance to abrasion with the growth of filling is reduced (which is natural, because graphene is a soft material), although at small additives there can be interesting effects (Table 5, see for 0,05 wt%) for strengthening of abrasion resistance.

Figure 5. Visual effects of the daily effect of acetone on samples without (H, Na) and with graphene (from ethanol solution, 8 g/L).

Table 6. Swelling in a acetone: ethyl acetate (1:1) of samples with 0.01-1 wt% of graphene.

	Unfilled	0.01wt%	0.1wt%	0.5wt%	1wt%
Mass of simple, mg					
0	280	200	200	310	170
0,0125	290	201	212	303	187
0,042	296	209	214	304	192
0,125	303	211	219	303	195
1	314	218	226	320	220
2	319	223	225	Destr.	Destr.
8	339	233	234		
100 days	359	254	252		

According classical literature (Zuev [20], on p. 71), crushing in aggressive media takes place due concentration of stresses on structure's defects. In addition to the energetic and diffusion factors, the development of cracks is determined by the relaxation processes at the boundary swollen/non-swollen polymer. The solvent causes the appearance of normal and tangential stresses in the sample. The tangential component relaxes slowly as a result of the resistance of the non-swollen nucleus at the center of the polymer, and stretch voltages appear in the swollen layer [18]. Cracking begins when the nucleus reaches the critical stress on the boundary "swollen polymer - a non-swollen core". This is aggravated by great rigidity (considerable stresses arise at small deformations) and a decrease in the diffusion rate (which contributes to the preservation of large stresses in the places of their concentration) [18].

3.3. Heat Resistance and Fire Resistance

The thermograms of the composites show that there is no special change in the thermal-oxidation destruction after graphene-filling as at low (0.05 wt%) as relatively large (2 wt%, when the composition becomes high-viscosity) fillings (Figure 6). The temperature of loss of 5% of weight after filling decreases significantly (from 270°C for uncharged to 240 for 2 wt%), and 10 wt% is insignificant (from almost 300°C to 280°C).

In acetone, epoxy-graphenes swells speedily, and destructs in 1-2 days. It is result of corrosion-crushing (cracking, figure 5) in acetone media.

The presence of graphene in the composite does not enhance the resistance to acetone (table 6), although it may lead to less active swelling in the first hours.

Figure 6. Thermogrammes (TG, DTA and DTG) of composites.

4. Conclusions

Graphene (0.01 – 5 wt%) is well combined with epoxy resin, giving relatively homogenous compositions with a micro-aggregate consistence of the filler.

Most of the examined strength parameters of composites after filling changed insignificantly. But substantial growth only adhesive adhesion to steel was observed - in 1.3-3.5 times (the stronger the higher the filling). At small additives

of graphene resistance to abrasion (0.05wt%) and compressive strength (0.01 wt%) can improve. Also, as the filling was growing, shrinkage decreased, disappearing to 5 wt% of filling. At 0.1 – 5 wt% of filling, the compressive strength is reduced with filling, and composite becomes more sensitive to the heating as the action of a strong oxidant.

The physico-chemical resistance of composites after more than 0.1 wt% of graphene was sharply reduced in acid-oxidizing (conc. HNO₃) and aggressive organic (acetone-ethyl acetate) media. The thermograms of the composites show that there is no special change in the thermal-oxidation destruction after graphene-filling as at low (0.05 wt%) as relatively large (2 wt%) fillings.

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