Analysis of the behavior of epoxy composites with carbon nano additives under the influence of high temperatures on fires

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Abstract. The results of research on the thermal stability of epoxy resins modified with carbon nanomaterial as polymer composites matrices are presented. It is shown that modification of binder component of composite materials at deposition of carbon nanomaterials leads to improvement of thermal stability, including decrease of intensity of crystal lattice destruction, decrease of amplitude value of thermal effect, increase of duration of oxidation of material at high temperatures, promotes stable formation of heat-protective and insulating carbonized layer.

1. Introduction
In modern conditions, the so-called composite materials (composites) are considered one of the most promising and most demanded materials. A separate niche of composites is occupied by polymer composite materials. In their design at least one continuous phase is an organic polymer - for example, epoxy resin (hereinafter - ER). However, polymer composite materials based on thermosetting binders, which include epoxy resins, have a number of essential characteristics that deter their active use. For example, they become more brittle when exposed to elevated temperatures, have low heat resistance, impact toughness [1].

Technologies based on the exploitation of composites face the problem of low thermal stability of epoxy resins. The mechanism of epoxy resin destruction at elevated temperatures is as follows [2]. First of all, epoxy groups are isomerized with the formation of the end aldehyde structure, with subsequent restructuring of the structure, acrolein is formed. The primary radical disintegrates into CH₃O molecule and CH₂=CH-O radical. The isomerization of this radical may result in the formation of acetyl CH-CN-O radical, which takes away hydrogen from the epoxy resin and forms acetaldehyde. Finally, the acetyl radical may disintegrate into CO and CH₃. This latter, by adding hydrogen, turns into methane. It is due to the ramified chemical structure of the substance that the problem of reduced stability of the material at elevated.

When assessing the strength of composites under thermal impact it is necessary to determine the temperature range of the thermal stability of the material. To compare the behavior of epoxy resins in the process of heating, it is reasonable to identify such criteria of thermo-oxidative degradation as the temperature at which mass losses of 5% and 10% are observed [3] and the maximum decomposition temperature [4].
It should be noted that epoxy can change its characteristics by introducing various modifiers into it [5]. One of the most promising methods for improvement of material performance today is modification of composite materials with different nanostructures. Among a wide range of nanomaterials, carbon nanostructures (hereinafter, CNTs) are favourably distinguished [6]. This material has an unusually high modulus of elasticity and tensile strength, constancy of physical properties at various temperatures, from cryogenic to hydrocarbon fire.

| Source | Type of nanoparticles + base material | Concentration of nanoparticles, % by mass | The observed effect |
|--------|-------------------------------------|------------------------------------------|-------------------|
| [7]    | MWNTs/epoxy system                   | 0.25 wt%                                 | The initial decomposition temperature clearly became higher with an addition of amino functionalized MWNTs, which increased about 30 °C from 361 °C to 392 °C by adding 0.25 wt% amino-functionalized MWNTs. |
| [8]    | VTES—CNTs + DGEBA epoxy resin        | 9 wt%                                    | The composite materials with 9 wt% CNTs content did not exhibit any obvious thermal transition. The LOI values of composites that contain 9 wt% CNTs are higher, 29, than that of pure epoxy resin, which is only 22. |
| [9]    | Nanocluster graphene oxide, Nanodiamond hybrid filler (GN) + epoxy matrix | 0.2-0.4 wt%                               | The incorporation of 0.2 wt% a-MWCNT provided a slight shift of thermal stability to higher values (around 2%) with respect to unfilled nanostructured matrices. This shift of thermal stability can be also observed by the increase in solid residue. |
| [10]   | Diglycidyl ether of bisphenol A (DGEBA) epoxy resin + a-MWCNT | 0.2 wt%                                  |                  |

Table 1. Analysis of conducted studies - properties of ER modified by CNTs.

Thus, when binding the components of epoxy matrixes used as modifiers for ANS with molecules, due to their antioxidant properties, there is an increase in strength characteristics and thermal resistance of materials. This, in turn, leads to an increase in the energy required to destroy a structured sample, which allows slowing down the destruction processes in the matrix [7-10].

This paper presents the results of the study of stability of epoxy resins under the influence of elevated temperatures to create technologies for the production and use of composites with an epoxy matrix modified by carbon nanostructures to improve the fire resistance of products based on these materials.

2. Experimental
2.1. Materials

The object of study was the thermal resistance characteristics of epoxy composite binder samples consisting of ED-20 epoxy resin, triethylene tetramine hardener (TETA), and diethylene glycol (DEG-1) diglycidyl ester plasticizer. The manufacturer of ED-20, TETA and DEG-1 substances is JSC «ENPC Epital», Moscow, Russia.

The modifiers were powdered carbon nanomaterials - astralen (hereinafter - Astr), produced by CJSC “Science and technology center of applied nanotechnologies”, St. Petersburg, Russia. According to [11], asterlenes are multilayer torus-like particles - polyhedral structures of carbon atoms - with the size of 15...150 nm. Astr is an innovative additive based on nanosized carbon.

The spectrum of Raman scattering of the modifier obtained at the NT-MDT NTEGRA Spectra (Figure 1) allows to judge about the presence in the substance as the main D-band, which is characteristic for all substances with carbon content, and G-band, which reflects the tangential fluctuations in the graphene layer plane (Table 2).

![Figure 1. Raman Scattering Spectrum Astr.](image)

| Substance                     | Oscillating range                                      | Bandwidth of spectrum, cm\(^{-1}\) |
|-------------------------------|--------------------------------------------------------|-------------------------------------|
| Astr                          | D-band carbon materials                                 | 1400                                |
|                               | G-band (tangential vibrations in the graphene layer plane) | 1646                                |

By analyzing the data obtained, we can conclude that the Astr is a form of carbon. This is also manifested by the fact that in nanoparticles one can observe the properties typical for a given chemical element, which include strength and structural characteristics [12-14].

The structure of the solid residue was examined by atomic force microscopy also on the NT-MDT NTEGRA Spectra by half-contact method. The samples of Astr solution were placed on a mica substrate and then the liquid evaporated at 70-80 °C for 10 minutes at normal atmospheric pressure. Then, the structure of dry residue surface was assessed. After evaporation of ethanol on an Astr solution mica substrate there were observed spotty carbon structures with the area up to 2×2 microns and accumulation of particles with the diameter of 0.5-1 microns (figure 2).
Figure 2. Picture of solid residue Astr, made on atomic force microscope.

Having analyzed the data, we can conclude that Astr is evenly distributed over its volume and also has small particle concentrations. This suggests that the stability of solutions of nanoparticles is quite high, which allows using them for modification of epoxy resins.

2.2. Sample preparation

At the first stage of preparation of the modified samples, suspensions were prepared on the basis of TETA hardener with the content of CNTs. This stage consisted in addition of carbon nanostructures into the volume of the hardener with their subsequent dispersion and was carried out at 20.0 (±0.2) °C and normal atmospheric pressure under the influence of an ultrasound source of 1 kW with a frequency of 60 kHz for 600 sec. In parallel, homogeneous suspensions of epoxy resin with plasticizer were prepared to create plasticized samples (at a ratio of ≈ 10:1). In the next stage, modified solutions of the hardener was added to the volume of pre-weighed resin to obtain compositions with concentrations of elements of 1-2 % wt., after which the resulting mixture was mixed for 300 seconds until a homogeneous state. At the stage of polymerization cold curing of the obtained compositions was carried out at room temperature.

2.3. Methods

In order to fully evaluate the behavior of the epoxy matrix of composite material under thermal conditions, a study of the thermal effect of modified polymerized resins using the thermal analysis method was conducted. Thermal analysis was carried out with the help of "Thermoscan-2" unit, heating of the sample was carried out from room temperature up to 600 °C with heating speed of 10 °C/minute.

3. Results and discussion

The analysis of the heating process of the investigated material on thermograms (figures 3,4) indicates the presence of several thermal peaks corresponding to the thermal effect (hereinafter - TE) of the resin components.

Table 3 shows the values of indicators describing the combustion processes of the components of the investigated samples.

Thus, on the basis of comparison of ER thermal analysis indicators without plasticizer, it can be noted that the rate of oxidation of the modified sample is lower than the rate of volatilization of thermal decomposition products, which tells us about the increase of thermal stability of the material due to the increase of time spent on the process of oxidation from the beginning to its transition to the process of self-ignition of the material. At the same time, for a sample with 1% mass. Astr amplitude value of TE ER is lower than similar values of the control sample, which indicates a decrease in the intensity of ongoing exothermic reactions.
The epoxy matrix with the addition of plasticizer behaves a little differently (figure 4).

**Figure 3.** Differential-thermal curves: – reference sample, – with a content of 1% wt. Astr, – with a content of 2% wt. Astr.

**Figure 4.** Differential-thermal curves: – plasticizer-rich, – with 1% wt. Astr and plasticizer, – with 2% wt. Astr and plasticizer.

**Table 3.** Differential Thermal Analysis of Heating Graphs of Epoxy Samples without Plasticizer.

| Samples | Pure ER | ER with 1% Astr | ER with 2% Astr | ER softener-coated with 1% Astr | ER softener-coated with 2% Astr |
|---------|---------|-----------------|-----------------|---------------------------------|---------------------------------|
|         | peak    | peak            | peak            | peak                            | peak                            |
| Temperature at which TE begins, °C | 51 | 315 | 48 | 313 | Not observed | 317 | 50 | 305 | 56 | 311 | Not observed |
| Temperature of maximum | 115 | 351 | 118 | 353 | Not observed | 562 | 111 | 336 | 116 | 334 | Not observed ** |
TE, °C
| Temperature of TE end, °C | 170 | 375 | 151 | 377 | * | 136 | 355 | 138 | 357 |
|--------------------------|-----|-----|-----|-----|---|-----|-----|-----|-----|
| Amplitude TE value, °C   | 2.78 | 2.2 | 2.37 | 1.88 | 2.33 | 2.48 | 1.41 | 2.73 | 2.08 |
| Peak width TE, °C        | 119 | 60  | 103 | 64  | >317 | 86  | 50  | 82  | 46  |
| TE form index            | 0.86 | 0.67 | 0.47 | 0.6  | -   | 0.41 | 0.61 | 0.37 | 1.00 |

* - up to 600 °C termination of exothermic reactions is not observed
** - there is only the beginning of the thermal effect at 321 °C, with a slight bend at reaching 332 °C.

When comparing the thermal analysis of the control sample of ER and ER with the addition of plasticizer, there is a decrease in all indicators, which tells us about the increase in flammability, increasing the rate of oxidation and burnout of the sample material, and as a consequence, a decrease in the stability of combustion when introducing a plasticizer based on diglycidyl ether diethylene glycol. This phenomenon is caused, first of all, by dilution of epichlorohydrin, which selfignition temperature exceeds 400 °C, by more combustible diethylene glycol with selfignition temperature 210 °C [15]. The problem can be solved by using plasticizing compounds with higher thermal protection properties of the coke layer formed on the surface.

Comparison of ER modifications with plasticizer shows significant shift and smoothing of the second characteristic TE peak. Such a gentle form and stretching of exothermic effects is typical for slow processes of oxidation - formation of coke layer - with subsequent coke burning and evaporation.

**Conclusions**

1. Due to the strength characteristics and reinforcement properties of Astr, which allows to cross-link the structural defects of the modified material, for samples with a content of 2% wt. Astr on thermogravimetry curves there are no peaks of thermal effect, that is, when the material is heated up to 600 °C crystal lattice failure is not observed.
2. When Astr modifiers with strong antioxidizing properties are introduced into the material structure, the oxidation process is slowed down. Increasing the duration of oxidation contributes to the formation of carbonized layer, contributing to thermal protection and insulation.
3. Due to the small size of particles Astr have a large specific surface, which determines their high sorption properties. Due to this, for samples with a content of 1% wt. Astr decreases the amplitude of the thermal effect.

The achieved results allow to concretize and supplement theoretical data on the behavior of epoxy matrixes modified by carbon nanostructures under the influence of elevated temperatures, and also demonstrates the positive effect of the modification on the thermal characteristics of epoxy material.

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