Fireproof intumescent systems modification by means of phosphorus-containing metal/carbon nanocomposites for construction applications

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Abstract. In the present paper, a method for modifying a copper/carbon nanocomposite with ammonium polyphosphate is considered. The optimum ratio of reagents at the modification of composite was found using infrared and X-ray photoelectron spectroscopy. Experimental tests were carried out for samples of fireproof intumescent coatings based on epoxy resins modified with the phosphorus-containing copper/carbon nanocomposites. An increase of more than 20% in such properties as adhesive durability and fire-retardant performance for the coatings modified with the above nanocomposites was determined.

1. Introduction
The protection of buildings against destructive effects of high temperatures and fire is the main part in the designing of any structures. The application of incombustible materials as well as the use of special fire resistant coatings seem to be the most widespread methods to ensure fire resistance of structures.

At present, fireproof intumescent coatings can be successfully introduced into construction materials because their volume increases several times while forming an incombustible low-conductivity layer. The basic efficient characteristics of such coatings are as follows:

1) multiple intumescences;
2) intumescent layer durability;
3) intumescent layer structure (pore forms and sizes) [1,2].

It should be noted that recently modification of intumescent coatings with nanosystems has become the most commonly used method for improving foam coke characteristics [3-5]. However, in turn, the corresponding nanosystems should be modified before using them for developing fireproof coatings.

For example, in work [6], novel flame retardant system for wood polymer composites was developed based on the combination of ammonium polyphosphate with phytic acid modified layered double hydroxide. In another examples [2] mechanical, thermal, fire and morphological properties of thermoplastic composites filled with fire retardants and microcrystalline cellulose were investigated in detail. In work [7] fire resistant properties of nano-structured intumescent coatings were investigated.

The aim of this work was to develop a method for modifying copper/carbon nanocomposites with ammonium polyphosphate for using in epoxy-based intumescent flame-retardant coatings.
2. Materials and methods

2.1. Materials

A copper/carbon nanocomposite (Cu/C NC) was synthesized at Izhevsk Electromechanical Plant “Kupol” JSC (Izhevsk, Russia) through a mechanochemical method. The image of the nanocomposites is presented in figure 1.

![TEM image of the Cu/C NC.](image)

Ammonium polyphosphate (APP; Wellchem, Quzhou City, China), having crystalloid phase II (with extent of polymerization $n > 1000$) was used for modification of this nanocomposite.

The polymeric base of the coating composition included the following components: ED-20 epoxy resin ED-20 (FSE Plant named after Y.M. Sverdlov, Dzerzhinsk, Russia), polyethylene polyamine (PEPA) as cross-linking agent (Uralchimplast, Nizhny Tagil, Russia), and APP (Wellchem). To achieve uniform dispersion with phosphorus, the nanocomposite was introduced as a fine-dispersed suspension in the PEPA.

2.2. Nanocomposite modification and fine-dispersed suspension production

The modification of the Cu/C NC with the APP was performed through mechanochemical interaction of the reagents using a mechanical mortar by adding a polar medium and, further, by heating the reactive mass for 3 min.

The process of fine-dispersed PEPA-based nanocomposite suspension production consists in preliminary grinding of the initial reagents in the mechanical mortar and further diluting (accompanied by mixing) to the required concentration. After these procedures, the obtained suspension is sonicated using a Volna-M USTA-1/22 dispenser (U-SONIC, Biysk, Russia) for 3 min for uniform volume-based size distribution.

2.3. Spectroscopic studies

Infrared (IR) studies were performed on a FSM 1201 (Infraspek Ltd, Saint-Petersburg, Russia) Fourier-transform IR spectrometer in the wave number region corresponding to 4000–650 cm$^{-1}$[5].

X-ray photoelectron spectroscopy (XPS) studies were carried out on an XPS magnetic spectrometer (PTI of Ural Branch of RAS, Izhevsk, Russia) in a way described in [8].
2.4. Studying the fireproof coating properties

2.4.1. Coating sample preparation for fire-retardant performance determination. Fireproof (or fire-retardant) parameters were determined according to the ASTM E-14-10 method. The tests were carried out with plate-form samples of the following sizes: length – 50-55 mm, width – 10-15 mm, and thickness – 1-1.3 mm. The fireproof composition was deposited over the correspondent plate. The layer thickness on each plate was 1 mm. The samples were cross-linked for 24 h under normal conditions.

2.4.2. Sample preparation for adhesive durability determination. The adhesion durability was determined to Russian National Standard (GOST) No. 14753-73. The experiments were carried out on steel plates under displacement efforts.

2.4.3. Fire-retardant performance determination. The tests were performed on the steel plates coated with the epoxy resins modified by the APP with the phosphorus-containing Cu/C NC \([\text{Cu/C↔P}] (3\times10^{-3} \%)\). For these tests, the flame of a gas burner was used.

3. Results and discussion

3.1. Cu/C NC modification conditions

The studies on the initial Cu/C NC show that it represents metal clusters associated with carbon fibers or metal clusters within the carbon shell consisting of 3-4 layers of carbon fibers. Each carbon fiber includes acetylene and carbine fragments with delocalized electrons on fragments joints. In other words, the nanocomposite obtained has active surface, which contains double bonds and delocalized electrons [3].

For the studies of the APP layers thickness influence on the metal cluster magnetic moment and electron structure at the modification, the following ratios of Cu/C NC and APP were used: 1 (NC): 0.5 (APP); 1 (NC): 1 (APP); 1 (NC): 1.5 (APP)

3.1.1. IR investigations. The fragments of the IR spectra depending on the Cu/C NC : APP ratios are presented in figure 2. The characteristics of spectra peaks are set in table 1. The peaks at 1072 cm\(^{-1}\) attributed to P-O-C groups are noted on all the spectra. In this spectrum the higher intensity of the above peak is found when the ratio of reagents is equal to 1 (NC) : 0.5 (APP). In this case there are decreased intensities for peaks corresponding to P-O-P group (904 cm\(^{-1}\)) and P=O bond (close to 1254 cm\(^{-1}\)). These data can evidence of a more extensive reaction between the Cu/C NC and the APP. In spectra of samples obtained at the ratio of 1 (NC) : 1.5 (APP) the peak in region 1006 cm\(^{-1}\) attributed to P-O bond appeared that may be indicative of the presence of APP groups.

In table 1, the comparison of peaks intensities for P-O-P and P-O-C groups as well as peaks intensities for P=O bond is given. The increased peak intensity for P=O bond at 1253 cm\(^{-1}\) in the spectrum of APP-modified Cu/C NC (i.e., Cu/C↔P) can be explained by the availability of oxygen atoms close to the phosphorus atom. These results correspond to the data obtained in the XPS studies.
Figure 2. Fragments of the IR spectra recorded for the Cu/C↔P NC at the NC : APP ratios: 1:0.5 (a), 1:1 (b), and 1:1.5 (c).

Table 1. Characteristics of IR spectra peaks for the Cu/C↔P NC samples obtained at the NC : APP ratios: 1:0.5; 1:1; and 1:1.5.

| N (peak) | Sample | Spectrum peaks characteristics | Groups and bonds attributed to peaks [9] |
|----------|--------|--------------------------------|----------------------------------------|
|          |        | Peak wave number, cm⁻¹ | Intensity | Half width |                                    |
| 1        | 1:0.5  | 911               | 0.0105    | 42.32     | P-O-P                               |
| 1        | 1:1    | 904               | 0.0118    | 51.67     | P-O-P                               |
| 1        | 1:1.5  | 895               | 0.0245    | 57.45     | P-O-P                               |
| 1        | 1:0.5  | 1073              | 0.0547    | 149.26    | P-O-C                               |
| 2        | 1:1    | 1072              | 0.0399    | 135.31    | P-O-C                               |
| 2        | 1:1.5  | 1073              | 0.0194    | 71.08     | P-O-C                               |
| 2        | 1:0.5  | 1254              | 0.0057    | 50.48     | P=O                                 |
| 3        | 1:1    | 1254              | 0.00904   | 48.37     | P=O                                 |
| 3        | 1:1.5  | 1253              | 0.02225   | 53.03     | P=O                                 |
3.1.2. X-ray photoelectron spectroscopic investigations. For the chemical bonds (bonds between metal atoms, carbon and phosphorus) formation mechanism in above systems, the spectra of inner levels such as C1s, O1s, Cu3s, P2p are investigated (figures 3 and 4, table 2).

According to figure 3, the phosphorus reduction process proceeds more extensively at a ratio 1:0.5 (with a decrease of the APP layer) that is explained by the increasing of electron quantization. The peak corresponding to energy EP2p equaled to 132.5 eV is attributed to C=N bond [10]. This fact can be explained by the interference which is increased because of the direct electromagnetic field formed at the annihilation. It is possible that the reduced The phosphorus is found between the carbon fibers of the mesoparticle shell.

![Figure 3. P2p spectra recorded for the Cu/C↔P NC. NC : APP ratios – 1:1 (a) and 1:0.5 (b).](image1)

![Figure 4. C1s spectra recorded for the Cu/C↔P NC. NC : APP ratio – 1:0.5.](image2)

In the investigation of the C1s spectra of the Cu/C↔P NC (figure 3) obtained at theratio of Cu/C NC : APP ratio of 2 (or 1:0.5) the spectra consist of three components: sp² hybridization for C – C bond (284 eV); sp³ hybridization for the same bond (286 eV) and also for C–H bond (285 eV). The third component corresponds to C–H bond in poly acetylene fragment of nanocomposite carbon shell. The intensities of the first and second components are close. Therefore, it is possible that the nanogranules of the Cu/C↔P NC has the spherical form. The intensity of C–H peak at the ratio being equal to 2 is three times higher than the intensities of peaks at other ratios used in this investigation. That effect is possible when the carbon shell deformation occurs with the increasing polyacetylene fragments in the surface layer.

It follows from the comparison of copper atomic magnetic moments (table 2) that the higher increase of the copper atomic magnetic moment (M_m, µB ) is achieved for the Cu/C↔P NC obtained at the reagent ratio being equal to 2 (M_m = 4.5 µB). At a ratio of reagents being equal to 1, the copper atomic magnetic moment decreases more than twice. This result can be explained by the decreasing electron quantization velocity at the Ammonium Polyphosphate layer thickness growth.
Table 2. Parameters of multiple splintering of Cu3s spectra in the nanosystems.

| Sample                | $I_2/I_1$ | $\Delta$, eV | $M_{m, \mu_B}$ |
|-----------------------|-----------|---------------|-----------------|
| Cu/C NC               | 0.2       | 3.5           | 1.3             |
| Cu/C↔P NC (1:1)       | 0.4       | 3.5           | 2.0             |
| Cu/C↔P NC (1:1.5)     | 0.4       | 3.5           | 2.0             |
| Cu/C↔P NC (1:0.5)     | 0.85      | 3.5           | 4.5             |

$I_2/I_1$ – the ratio of multiple splintering lines maximums intensities; 
$\Delta$ - energetic distance between the multiple splintering maximums in Me3s spectra.

On the basis of above investigations, the optimum ratio of initial reagents is the ratio equal to 2. According to IR spectra and XPS studies, the reaction between the Cu/C NC and the APP proceeds more completely with the maximum growth of copper atomic magnetic moment.

3.2. Studying fireproof intumescent coatings modified with the phosphorus containing copper/carbon nanocomposites

A set of laboratory experiments on comparing the modified coatings with the initial ones were carried out, and the effect of the phosphorus-containing copper/carbon nanocomposite on the physical-mechanical characteristics and fireproof efficiency of the obtained coatings was assessed.

3.2.1. Determining the coating adhesive durability.

For the determination of the Cu/C NC introduction efficiency the following compounds were prepared:

1) ED-20+APP (20 %) with PEPA (reference sample);
2) ED-20+APP (20 %) with fine-dispersed suspension of Cu/C NC;
3) ED-20+APP (20 %) with fine-dispersed suspension of Cu/C↔P NC.

The quantity of Nanocomposites introduced to compositions equalled to 0.1 %. This quantity of nanocomposites is considered as the maximum for achieving a positive effect without negative consequences. The diagram of the adhesive durability dependence on the composition and forms of the coatings is presented in figure 5.
Figure 5. A dependence of the adhesive durability of the samples on the coating content.

According to above diagram, the introduction of the Cu/C↔P NC into the coating composition increases the adhesive durability by 22 % as compared to the fireproof coatings without this nanocomposite.

3.2.2. Fire tests of a fireproof coating. The photos of the fireproof coating samples before and after the fire tests are presented in figures 6(a) and 6(b), respectively. The height of foam coke was measured from the steel plate surface to the upper level of the foam coke layer. The dependence of the foam coke height on the coating content is given in figure 7.

Figure 6. Photos of the samples before (a) and after (b) the fire tests.

As can be seen, the height of the Cu/C↔P NC-modified foam coke sample was found to be 28 % greater than that of the initial sample. Thus, one can assume that the introduction of phosphorus in the form of ammonium polyphosphate into the nanocomposite increases the activity of the latter.
4. Conclusions

For the first time, phosphorus-containing copper/carbon nanocomposites were synthesized through activation and mechanochemical modification. In this case, the change of element oxidation states, as well as an increase of the copper atomic magnetic moment, takes place. At the same time, the elements and functional groups with them appear in the carbon shell of the nanocomposites. These facts open a new era for further investigations and development of metal/carbon nanocomposites as well as searching for their possible application fields. For instance, the application of these active nanosystems to obtain fireproof intumescent coatings containing epoxy resins and ammonium polyphosphate seems to be promising, since they increase the adhesive durability by 22 % compared to the fireproof coatings without nanocomposite introduction, furthermore, the height of foam coke samples, which are modified by means of the phosphorus-containing copper/carbon nanocomposite, is 28 % greater than that of the unmodified samples.

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