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STUDYING THE STABILITY OF AQUEOUS SUSPENSIONS OF MULTIWALLED CARBON NANOTUBES USED FOR THE MODIFICATION OF COMPOSITE MATERIALS

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Abstract. In this paper, the stability of aqueous suspensions of multiwalled carbon nanotubes (MWCNTs) has been studied with physical and chemical methods. The optimum dispersion time of MWCNT suspension in a rotary homogenizer has been found. The dispersion time being increased, the quality of the suspension decreases. The data of the physical and chemical studies has also been confirmed experimentally on gypsum samples. The samples modified with MWCNT suspension of 2-hour dispersion show an increase in flexural strength and compressive strength by 40% and 48%, respectively, in comparison with the control sample, whereas the samples modified with MWCNT suspension of 10-hour dispersion show a decrease in flexural strength and compressive strength. The microstructure of the gypsum samples was studied with a scanning electron microscope.

Keywords: multiwalled carbon nanotubes, suspensions, microstructure, IR-spectral analysis, differential scanning calorimetry, dispergation.

Introduction

Currently, there is a problem of producing materials with the improved thermal and physical and/or improved physical and mechanical characteristics. A promising way to improve the properties of building materials is the use of carbon nanotubes as a modifying agent. Carbon nanotube (CNT) was firstly documented by Iijima in 1991 (Iijima 1991). Since then, the investigations related to CNTs and CNTs-based various composites have been extensively and intensively carried out owing to their excellent electronic, mechanical, and thermal properties (Wong *et al.* 1997). The first mention of the possibility of their application in construction was in 2003 in paper (Makar *et al.* 2003), where the authors showed the possibility of using CNTs as crystal seeds in the hydration process of cement. Since that time the construction material study has been showing a growing interest in carbon nanostructures, which is reflected in a large number of both foreign and domestic publications. Paper (Weitzel *et al.* 2011) also shows the effect of carbon nanotubes as crystallization nucleus of cement hydration products. The method of adding carbon nanomaterials for the enhancement of composites is protected by U.S. patent (Ogden 2006). Papers (Maeva *et al.* 2009) study dense structure concrete based on Portland cement modified with MWCNTs.There is a significant increase in flexural strength of fine-grained concrete by 45.1% and by 96.8% in compressive strength. The improved strength of concrete can be connected with the change of the morphology of crystal hydrate new formations which provide the formation of low-defect

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cement matrix structure of the increased density. In paper (Yakovlev *et al.* 2013) it is noted that adding the dispersion of multiwalled carbon nanotubes (MWCNT content is 0.006% of the mass of the binder) in silicate aerated concrete stabilizes the microstructure of gas silicate providing the uniformity of pore size and their distribution in material.

This increases strength and durability as well as improves thermal performance of aerated concrete. A significant change in the physical and mechanical properties of concrete was reached by researchers (Sanchez, Sobolev 2010) by adding ultralow dose of dispersed multiwalled carbon nanotubes 0.006–0.042% from the mass of cement. Thus, physical and mechanical properties of materials can be significantly improved by adding ultra-low percentage content of nanostructures (hundredths or thousandths) due to their high activity. The problem of uniform distribution of such ultra-low amounts of substances in the body of material is solved with using aqueous suspensions of carbon nanotubes. The suspensions should be stable in time as well as retain the activity of nanostructures. Also the process of preparing suspension is very important, as it is this stage where its main properties are determined. However, currently, this has not been studied enough as the dependencies of changes of its properties and the suspension quality on the technology of its dispersion have not been established.

1. Experimental part

The research object is MWCNT and their suspensions. The MWCNTs used were those of Graphistrength™ Masterbatch CW 2–45 of Arkema, a French chemical company, which consist of 10–15 layers of nanotubes with an outer diameter of 10–15 nm, from 1 to 15 microns in length, and an average density of 50–150 kg/m^3. This product is a granular dispersed mixture of multiwalled carbon nanotubes in carboxymethyl cellulose medium containing 45% of MWCNTs.

Due to excessive activity, sedimentation stability of MWCNT in liquid is quite low. Therefore, in order to obtain a stable suspension, the conditions are to be created that would lead to phase separation and decrease of coagulation of carbon nanotubes in suspension. Extensive external influence is required for separation of particles agglomerates of nanotubes, for example, ultrasonic treatment or treatment in a high speed mixer of rotary type (Deryagin *et al.* 1985). The protection against coagulation can be an adsorption-solvation layer on the surface of nanotubes which prevents them from approaching. The best option is to use surface-active substances (Holmberg *et al.* 2007). Li *et al.* (2007) used sonication of multiwalled carbon nanotubes in a solution of sulfuric and nitric acids (functionalization) to improve the bonding between MWCNTs and cement matrix. Cwirzen *et al.* (2008) to obtain homogenous dispersions of MWCNTs in water used polyacrylic acid at ultrasonic treatment. Their adding results in a decrease of interfacial surface energy and facilitates dispersion (Rebinder 1979; Gorjunev *et al.* 1966). Carboxymethylcellulose is a surfactant for carbon nanotubes. Being adsorbed at the interface of nanotube – water, carboxymethylcellulose reduces the surface tension on the surface of nanoparticles, which prevents them from coagulating into larger formations.

To analyze the degree of dispersion and stability in time the samples of aqueous suspensions of carbon nanotubes (CNTs content 9%) with different dispersion time of 2, 4, 6, 8, 10 hours were selected. The disperser of suspension was a rotary homogenizer: Silverson L4RT grinding system and high-speed bead mill developed by "Novyy Dom", Ltd (Izhevsk, Russia) (Pudov 2013).

To analyze the structure and properties of the investigated suspensions modern methods of physical and chemical research were applied. A set of analysis methods provides a comprehensive research of suspension morphology and its changes.

IR spectral analysis was performed on IRAffinity-1 Fourier spectrometer of Shimadzu within the range of wave number of 4000 to 400 cm^{-1}.

The microstructure was researched with a scanning electron microscope of Phenom G2 Pure at the magnification of up to 7500 times.

Thermal analysis was conducted using differential scanning calorimetry equipment and thermogravimetric analysis of TGA/DSC1 manufactured by "Mettler Toledo", JSC, at the temperatures from 100 to 800 °C and with a lifting rate of 20 °C/min. This device provides joint conducting of thermogravimetric analysis and differential scanning calorimetry and obtaining thermogravimetric curve (TGA) and differential scanning calorimetry curve (DSC).

To confirm the results obtained by physical and chemical research methods, the experimental studies with gypsum samples were carried out.

2. Results and discussion

IR-research of suspensions. The most interesting range is within the wave numbers from 950 to 1220 cm^{-1}. It is in this region where there is oscillation of C–O polar bond which is typical for cellulose ethers – carboxymethylcellulose (Smit 1982) (Fig. 1a).

The analysis of suspensions spectra shows that in the given frequency range there are differences in the intensity of absorption. Significant differences are observed for suspensions of two- and ten-hour dispersion (with gradual change of suspensions for four-, six-, eight-hour dispersion) (Fig. 1b, Fig. 2, Fig. 3a). In the IR spectrum of suspension dispersed for 2 hours the intensity absorption line corresponds to the absorption line in the spectrum of carboxymethyl cellulose (i.e. fluctuations in this region correspond to the oscillation vibration of C-O polar bond) (Fig. 1b).

In the spectrum of the suspension dispersed for 10 hours in the studied field the intensity line correlates with the absorption line in the spectrum of Masterbatch CW 2–45 carbon nanotubes (there is absorption line corresponding to the oscillation of C-O polar bond) (Fig. 3b).

This can be explained as follows: for two-hour dispersion of suspension there is no destruction of adsorption-solvate layer, i.e., carboxymethyl cellulose from the surface of carbon nanotubes, but with the prolonged C–O bond of carboxymethyl cellulose is broken, so the absorption line is missing.

Thermal analysis of suspensions. Degradation of CMC in suspension dispersed for 2 hours occurs at the temperature of 314 °C (Fig. 4), in suspension dispersed for 6 hours at 297 °C (Fig. 5). Carbon which is formed due to CMC destruction stimulates the oxidation of carbon nanotubes with their full burn at the temperature of 493 °C, while carbon nanotubes in suspension with the processing time of 2 hours undergo complete degradation at the temperature of 600 °C.

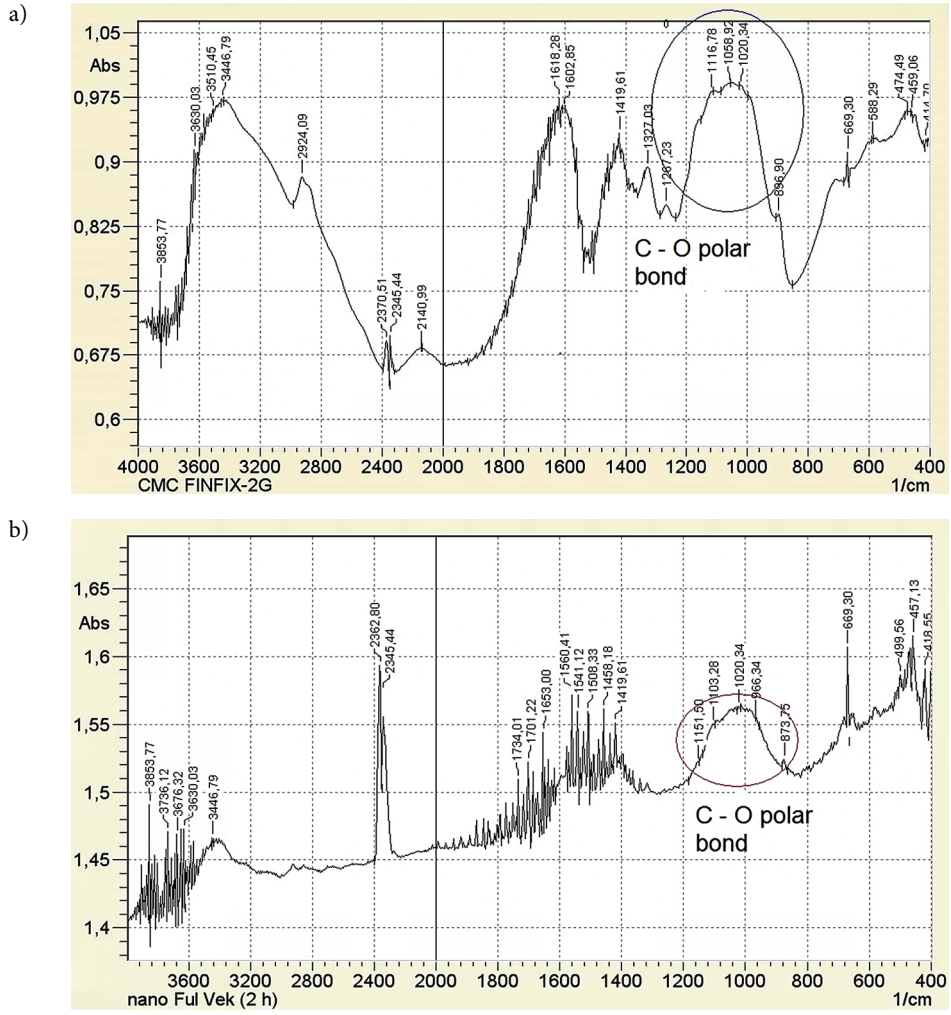

Fig. 1. IR spectrum of adsorption: a – of carboxymethylcellulose; b – of suspension processed for 2 hours

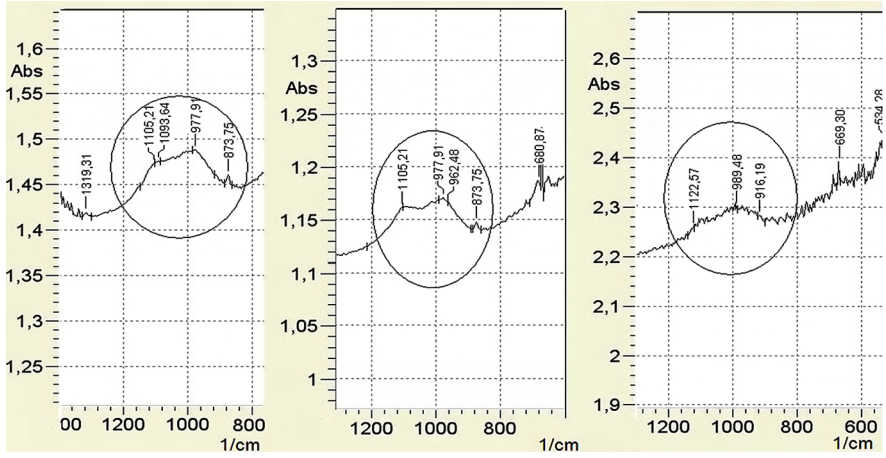

Fig. 2. IR spectrum of suspensions being treated for 4, 6, 8 hours in the considered interval (from left to right)

a)

b)

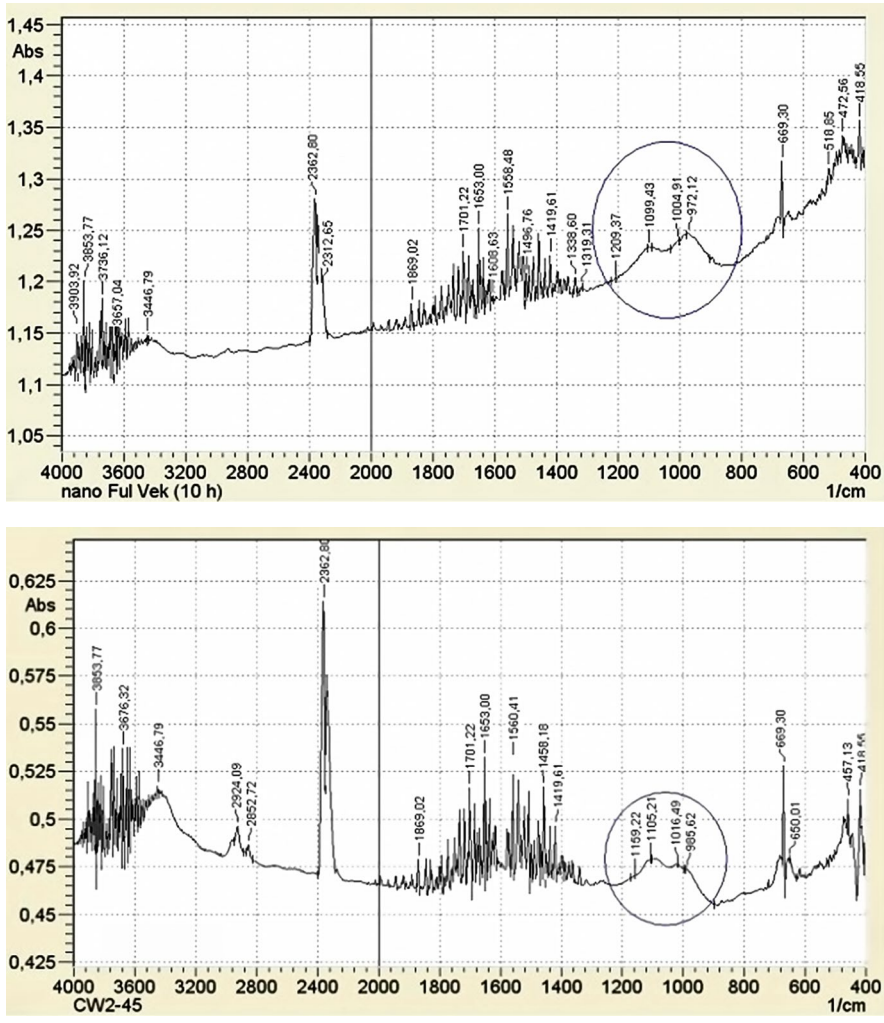

Fig. 3. IR spectrum: a – of suspension treated for 10 hours; b – of Masterbatch CW 2-45 MWCNTs

Thus, the data of thermal analysis shows suspension segregation during the long treatment in disperser for more than 2 hours.

Microscopic study of suspensions. In the picture of the suspension microstructure dispersed for 2 hours (Fig. 6a), no large CMC aggregates are present as CMC molecules are spread on the surface of the nanotubes as a thin layer. The picture shows the microstructure dispersion treated for 4 hours in a mixer, and partial CMC conglomerates is observed due to their exclu-

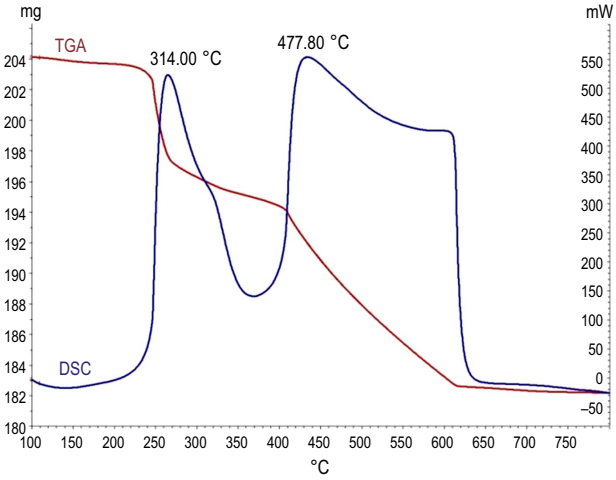

Fig. 4. Curves of DSC suspension treated for 2 hours in mixer

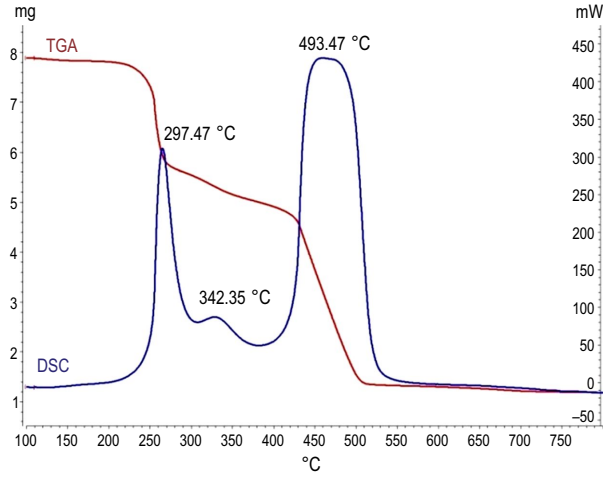

Fig. 5. Curves of DSC suspension treated for 6 hours in mixer

a) b) c)

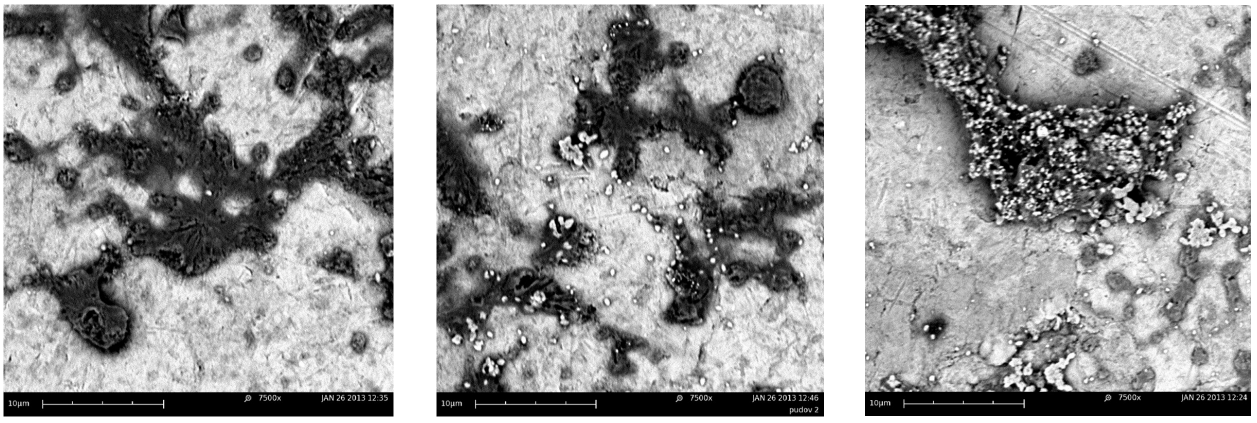

Fig. 6. Microstructure of suspension treated for: a – 2 hours; b – 4 hours; c – 10 hours at 7500-time magnification

sion from the nanotube surface (Fig. 6b). The dispersion time of nanotube suspensions being increased, the number and size of CMC conglomerates on the surface of multiwalled carbon nanotubes was found. The macrography of suspension treated for 10 hours in a mixer (Fig. 6c) shows that carbon nanotubes are completely coated with coagulated CMC particles.

MWCNTs suspensions of 2- and 10-hour dispersion were tested with gypsum samples. The mechanical tests were applied to control samples (containing 0% of MWCNT), modified samples with MWCNT content in the amount of 0.001–0.01% from the mass of the binder. These mechanical testings are presented in Figure 7. The samples modified with MWCNT suspension of 2-hour dispersion showed the increased bending strength and compression strength by 40% and 48% respectively. While the samples modified with MWCNT suspension of 10-hour dispersion showed no change in the bending strength, the compressive strength was decreased by 14%.

Figure 8 a shows the microstructure of the gypsum control sample. The analysis of the gypsum sample microstructure without MWCNT showed that lamellar crystals are randomly distributed in matrix forming high-porosity structure. The gypsum composition with MWCNT suspension dispersed for 2 hours one can see some dense areas without microcracks, which means that MWCNT act as crystallization centers, on whose surface a large amount of gypsum dihydrate crystals are formed (Fig. 8b). This leads to a increase of mechanical strength.

The picture of the gypsum sample modified with MWCNT suspension of 10-hour dispersion shows close pack dense areas, but with a large number of microcracks (Fig. 8c). In the picture one can also see some large pores. This can be explained by the fact that MWNTs form large conglomerates, thus acting as a foreign substance.

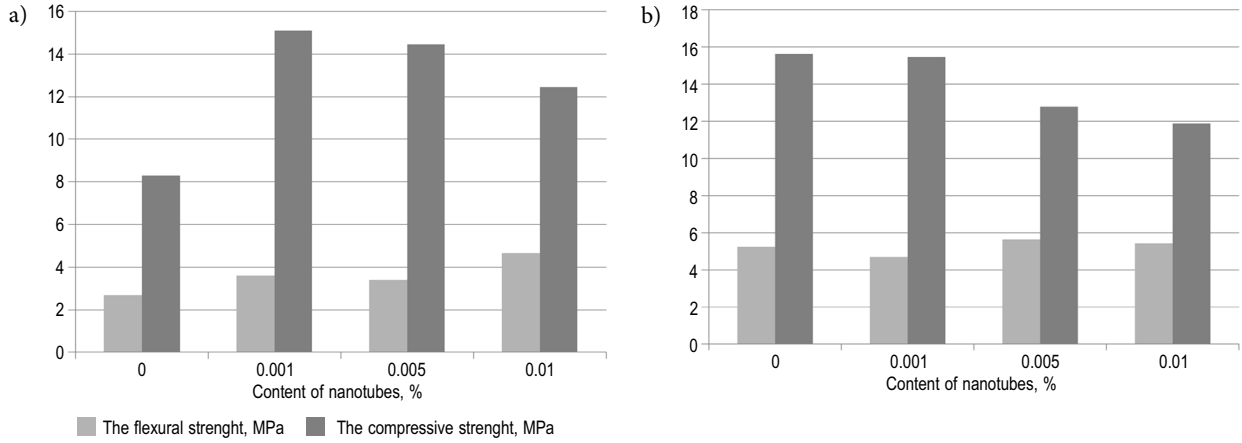

Fig. 7. Gypsum matrix durability with addition of suspension of MWCNT dispersed within: a – 2 hours; b – 10 hours

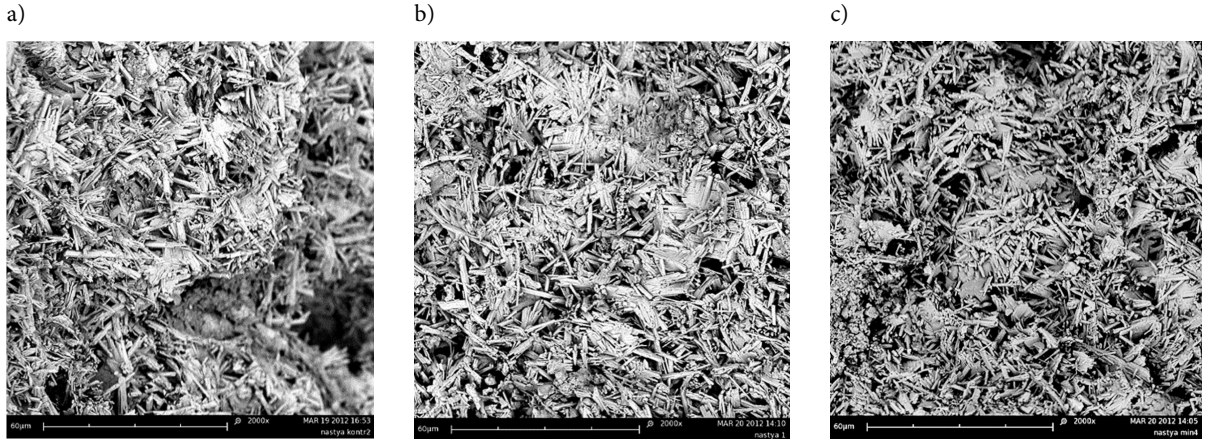

Fig. 8. Microstructure of the gypsum sample: a – control; b – modified with CNT suspension of 2-hour dispersion; c – modified with CNT suspension of 10-hour dispersion

Conclusions

1. Long lasting dispersion (over two hours) adversely affects the quality of MWCNTs suspension. The dispersion time being increased, a layer of carboxymethylcellulose on the surface layer of carbon nanotubes decreases up to its destruction. Thus recoagulation of nanotubes occurs to form larger balls and granules, which is undesirable because of the resulting loss of efficiency that occurs when modifying building materials are modified and its stability in time decreases.
2. In the gypsum composition modified with MWCNT suspension of 2-hour dispersion carbon nanotubes act as crystallization centers, which leads to a significant increase in bending strength and compressive strength.

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