POSSIBILITIES OF DISPERGATION OF CARBON NANOTUBES IN AQUAEOUS SOLUTION

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Abstract

This paper deals with very popular topic of using nanomaterials in building industry. Of all current scientific areas, nanotechnology has the fastest developement and biggest potencial. Some say that its impact will be even more important than discovery of steam engine or penicillin. Out goal was to analyze the possibilities of dispergation of carbon nanotubes (CNT) in aqueous solution and cementitious matrix. The basic properties of carbon nanotubes are extreme tensile strength and Young's modulus of elasticity, high aspect ratio and huge specific surface area. Because of this, CNT tend to aggregation and cluster formation. When load is applied on the composite, those clusters behaves like filler with very poor mechanical properties, causing decrease of both tensile and compressive strenght. Perfect dispersion of CNT is essential to avoid this problem. Experimental part of this paper is aimed to dispersion of carbon nanotubes in aqueous solution with use of proper surfactant to produce stable suspension. To achieve this, magnetic stirring and ultrasonication was used. The quality of dispersion was examined through ultraviolet and visible spectroscopy and scanning electron microscopy. Samples of cement mortar reinforced with carbon nanotubes were made and their tensile and compressive strength in the age of 7 and 28 days was tested.

Keywords: Carbon nanotubes (CNTs), ultrasonication, dispergation, ultaviolet and visible spectroscopy

1. INTRODUCTION

More than two decades are carbon nanotubes (CNTs) in the centre of interest scientists across all parts of sciences. CNTs abounds excellent physical-mechanical properties. Their utilization in ordinary used building materials can make great impact for building industry and other part of human interests. If their incorporation to the cement matrix will be successful we can save amount of processed cement or build thin and environmentally friendly constructions. But there are still unsolved troubles with flawless dispergation, mixing with water and reagglomeration of CNTs. In this article we tried to puzzle out some problems with nanotubes. Namely we tried to create stable dispersion of CNTs and water through ultrasonic homogenizer Bandelin Sonopuls HD 3200. Four levels of homogenization energy was chosen. From dispersion of CNTs and water, sand and cement were produced specimens of cement mortar for testing impact of addition CNTs on the physical-mechanical properties. Reagglomeration was examined through UV-Vis spectroscopy with compared of blind sample and on samples from cement mortar through SEM.

2. CARBON NANOTUBES

Carbon nanotubes can be described as graphene sheets folded in cylindrical shape with length 10 – 100 μm and diameter in tens of nm. It is known their divide according to quantity of carbon sheets to single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). SWCNTs have internal diameter to 5 nm. In case of break of carbon sheets by external influences, decrease of expected positive influence on properties will happen. MWCNTs have internal diameter from 1.5 to 15 nm and external diameter to 50 nm. MWCNTs contains up to 50 layers of graphene sheets. Because of large number of carbon sheets, influence on physical-mechanical properties in case of their damage are not as big as when SWCNTs are used. [1] The first identification of CNTs were by japanese scientist Sumio Iijima in 1991. Till that time three possible ways how to produce nanotubes are well known: electric arc discharge, laser ablation, chemical vapor deposition (CVD). [2] CNTs have exceptional physico-mechanical properties with strength up to tens of GPa and Young modulus of elasticity up to 1 TPa. [3]

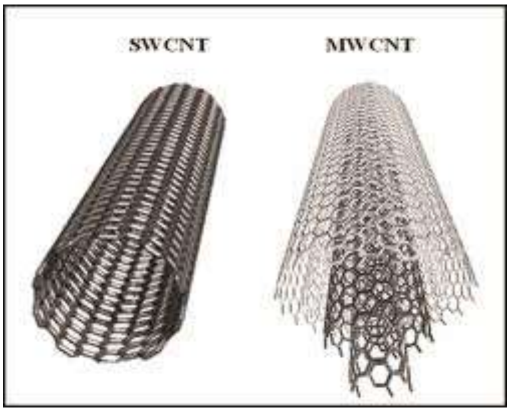

Fig. 1: Single and multiwalled carbon nanotubes [4]

3. DISPERGATION OF CARBON NANOTUBES

Perfect dispersion of carbon nanotubes in aqueous solution is the essential factor for their incorporation to the cement matrix and their expected effect to the characteristics whole composite material. Between carbon nanotubes exist strong Van der Waals forces which in combination with their big surface area and very high aspect ratio tend to attract each other and form clusters.The first presence of cracks during load are located to the clusters. This effect lead to decrease monitored physical-mechanical characteristics below value of samples not modified by CNTs. There are known ways of dispergation CNTs by use: sonication, mechanical (ball mill), chemical (surfactant) and their combination. Collins in his study combined dispergation by sonication with use appropriate surfactant. Results of his experiment indicate positive effect of combination sonication and appropriate surfactant not only to physical-mechanical properties, but also to effect of stability of CNTs in aqueous solution and their reagglomeration. According to results of Collins experiment it is possible to say that surfactants which have positive effect on stability of aqueous solution and extend time to reagglomeration are on the base of polycarboxylate and lignosulphonate. By suitable mode of mixing the positive results of physical-mechanical properties on samples of cement mortar were achieved. The 25 % increase of compressive strength compared to not modified samples was observed. It is very important to pay attention of using only surfactants which have not impact to hardening of cement mortar. [5] Also it is important to say that CNTs can be enriched by surfactants already from production. [6] Mendoza in his experiment pay attention destruction of structures of CNTs, when specific value of sonication energy was used. Due to results of his research it can be said, that CNTs can be damaged by high value of sonication energy. This lead to degrading their physical-mechanical properties and shortening them (decrease value of aspect ratio). Equally important is controlling and monitoring temperature of aqueous solution in which sonication take place. [7]

4. EXPERIMENTAL PART

Main aim of experimental part was dispergation carbon nanotubes in aqueous solution by sonication and their incorporate into cement mortar. Quality of dispersion CNTs was measured through ultraviolet and visible spectroscopy on samples of aqueous solution and scanning electron microscopy on samples of cement mortar. On samples of cement mortar was also examined compressive and tensile strength according to [8]. In available literature is dosage carbon nanotubes around 0.0025 - 0.1 % from dosage of cement, what is quite wide spectrum. It was decided that dosage of CNTs will be 0.005 % from dosage of cement.

4.1 Used materials

Multiwalled carbon nanotubes from Arkema Graphistrength CW2-45 were used. MWCNTs are there in 2% aqueous solution (contains 45 % of multiwalled carbon nanotubes and 55 % CMC - carboxymethyl cellulose). [6] As surfactant was utilized commonly used superplasticizer from Mapei on base of naphthalene with polymer chain. [9] As a binder was used portland cement from production of Mokrá (HeidelbergCement Česká republika). Normalized sand CEN EN 196-1 was utilized as a filler.

4.2 Apparatus

For primary mixing and homogenization of suspension was utilized magnetic stirrer Variomag monotherm with possibility of controlling of temperature and speed. For the purpose of dispersion suspension of CNTs, surfactant and water was used ultrasonic homogenizer Bandelin Sonopuls HD 3200 with power 200 W and possibility of controlling time , power and supply value of energy to homogenization. Other accessories to homogenizator was titanium probe and rosett cell. [10] Samples of cement mortar were prepared on Hobart's laboratory mixer.

Fig. 1: Ultrasonic homogenizator Bandelin Sonopulse HD 3200 [10]

Fig. 2: Magnetic stirrer Variomag monotherm

4.3 Manufacturing process

First step of manufacturing was homogenization through magnetic stirrer. Solution of water, CNT and superplasticizer (if it was used) was mixed for 5 minutes. After this step it was sonicated with ultrasonic homogenizer for defined time and power. Composition of concentrated solution for 100 ml is in Table 1. After termination of sonication concentrated solution was diluted with water for required volume of 600 ml. From this specimen was removed samples for UV-Vis spectroscopy. Samples of cement mortar were prepared on Hobart mixing machine. Specimens were embedded to water and examined after 7 and 28 days. Design of cement mortar was according to [8].

Table 1 Composition of concentrated solution of volume 100 ml

Sample	**Dosage of suspension [g]**			
	Water	**Superplasticizer**	**CNTs 2% solution**	**Homogenization energy [kJ]**
0.005-0.000-10	100	-	3.00	10
0.005-0.000-20	100	-	3.00	20
0.005-0.000-30	100	-	3.00	30
0.005-0.000-40	100	-	3.00	40
0.005-0.005-10	100	0.06	3.00	10
0.005-0.005-20	100	0.06	3.00	20
0.005-0.005-30	100	0.06	3.00	30
0.005-0.005-40	100	0.06	3.00	40

Note: key for reading marking of samples: dosage of CNTs [%] - dosage of superplasticizer [%] - homogenization energy [kJ]

5. RESULTS AND DISCUSSION

Values of absorbance between samples with and without superplasticizer were different. It could be due to addition of superplasticizer and its own impermeability for light or bigger dispersion of CNTs causing of superplasticizer. Variations of values of absorbance we can see in Fig. 3.

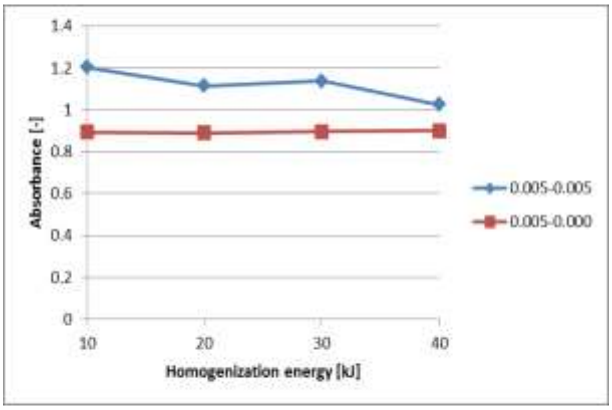

Fig. 3: Values of absorbance samples with and without addition of superplasticizer

Values of tensile strength after 7 days showed incredible increase, but after 28 days were values of strength almost same and in case of samples with addition superplasticizer even lower than reference samples. It could be explained by the fact that CNTs in some cases can operate like crystallization nucleus and accelerate the initial phase of hydration of cement. Values of compressive strength after 7 days showed slight decrease samples without addition of superplasticizer (SP), but after 28 days compressive strength samples with and also without SP were increased.

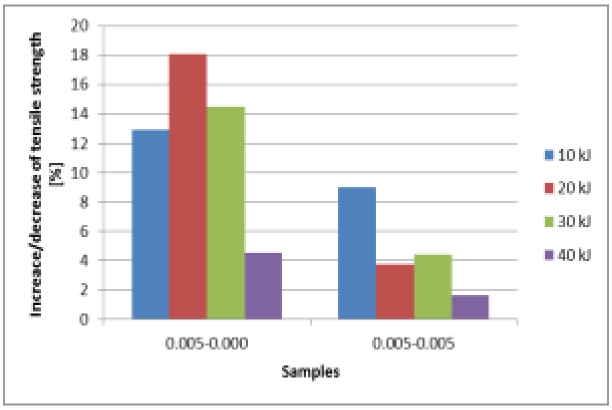

Fig. 4: Graphic interpretation of splitting tensile strength after 7 days

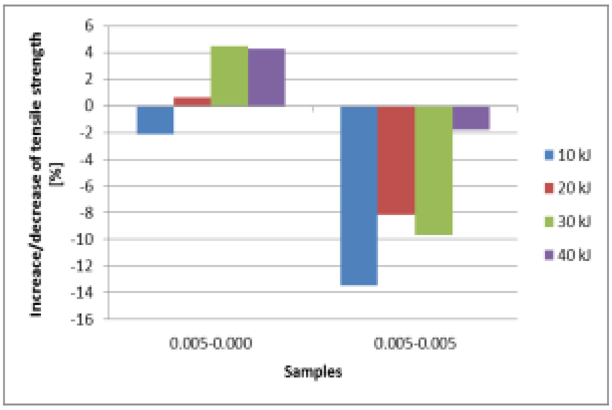

Fig. 5: Graphic interpretation of splitting tensile strength after 28 days

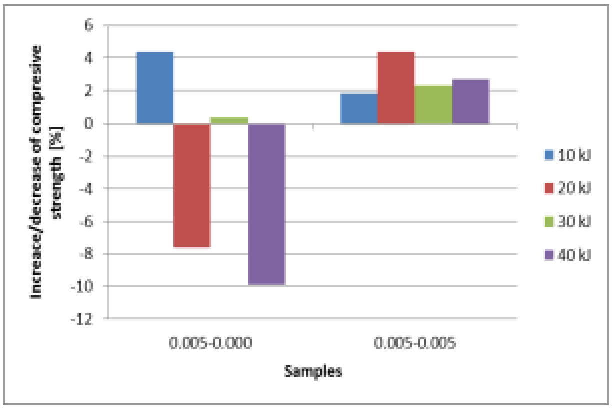

Fig. 6: Graphic interpretation of splitting compressive strength after 7 days

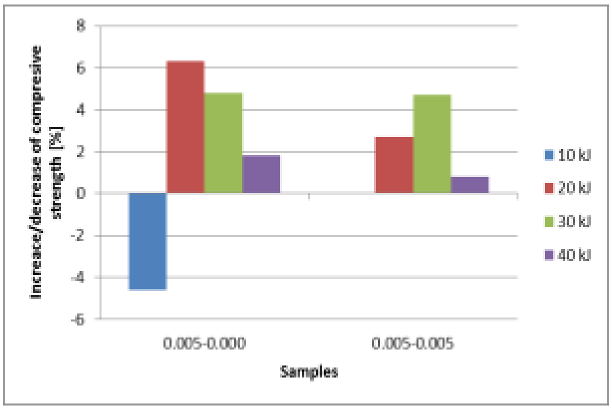

Fig. 7: Graphic interpretation of splitting compressive strength after 28 days

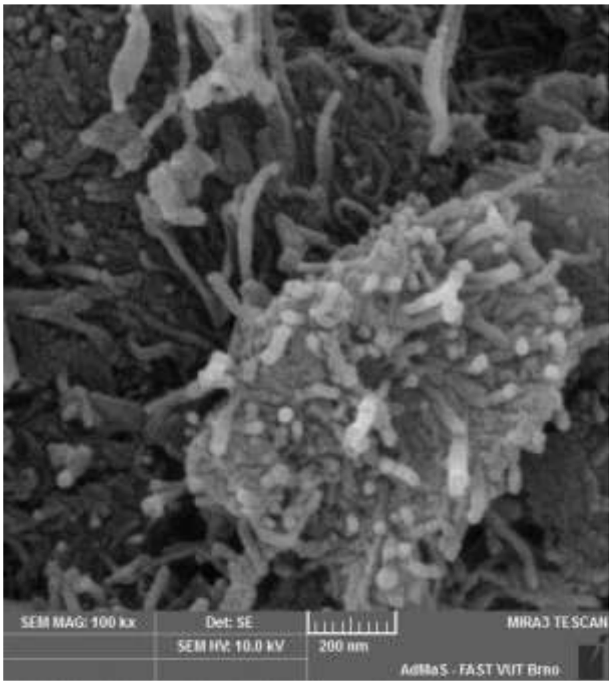

Fig. 8: SEM picture of CNTs (scale up 50000 times)

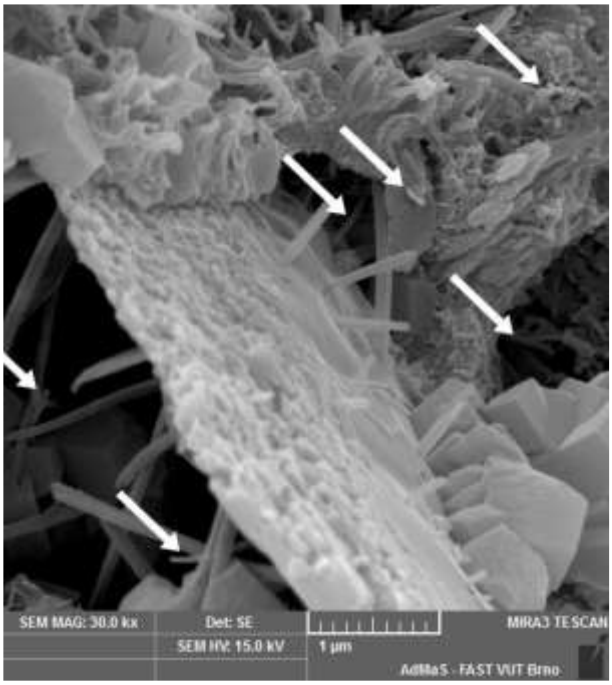

Fig. 9: SEM picture of CNTs (white digit); (scale up 30000 times)

CONCLUSION

Results of examined physical-mechanical characteristics does not confirm expected increase in addition of CNTs. It can be explained utilizing superplasticizer based on naphthalene and its supposed compatibility with CNTs. Another experiments indicate, that better compatibility of system superplasticizer, water and CNTs will happen when superplasticizer based on polycarboxylate will be used. Examined dispersion of aqueous suspension through UV-Vis spectroscopy provides interesting results, but it will be better to combinate this method with some other optical method for achievement understateble results. Ultrasonic homogenization can provide required dispersion of CNTs, but the right parameters of homogenization energy and surfactants will have to be setup. This article maybe give us more questions than answers, but it shows the way, where we can find them. Another research will be focussed on find suitable surfactant and possibilities of mixing suspension CNTs and surfanctant with bigger amount of water and its influence to stability of whole system CNTs-surfactant-water.

ACKNOWLEDGEMENTS

This outcome has been achieved with the financial support of project Junior specific research FAST-J-14-2550:"Study of possibilities dispersion of CNTs and their incorporate to cement mortar" and with the financial support of the European Union's "Operational Programme Research and Development for Innovations", No. CZ.1.05/2.1.00/03.0097, as an activity of the regional Centre AdMaS "Advanced Materials, Structures and Technologies".

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