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Applying multiwall carbon nanotubes for soil stabilization

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Abstract

The chemical stabilization of a soil is a technique where the soil is mixed with cementitious material in order to improve its mechanical behavior. The chemical stabilization is dependent on a wide range of parameters, being the most important ones associated to the soil properties and cementitious material characteristics. The nanoparticles are not a cementitious material but once introduced in a soil they are expected to reduce the interparticles' spacing, which will promote the construction of a stronger and stiffer soil skeleton matrix together with the cementitious material, therefore improving the mechanical properties of the soil. Thus, optimization of nanoparticles distribution is required to obtain a final material with the best characteristics at a competitive cost. In order to maximize the benefits of the nanoparticles (multiwall carbon nanotubes, MWCNT) added to a stabilized soil it is crucial to overcome the problems related with particle agglomeration. Thus, it was defined a strategy which comprises the characterization of the MWCNT (zeta potential and size), the definition of the aqueous medium with surfactant addition (a plycarboxylate-based surfactant was tested), the characterization of the surfactant (viscosity, molecular weight, zeta potential and molecule size) and the application of energy (with a particular power and during a specific time) to promote the particles' dispersion. The quality of the suspension, in terms of particles' dispersion, was evaluated trough the analysis of the particle size distribution given by dynamic light scattering (DLS). After, a series of performance tests (unconfined compression strength, UCS) test with the soil were conducted over samples with 7 of curing time. The preliminary results of the performance tests have shown the high potential of adding multiwall carbon nanotubes to a chemically stabilized soil. The results have also pointed out the importance of the nanoparticle homogenization process where the presence of the surfactant has a major role.

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Keywords: Carbon Nanotubes; Soil Stabilization; Particles' Dispersion; Dynamic Light Scattering; Surfactant

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1. Introduction

The economic development of modern societies in conjunction with the progressive concentration of the world's population and of industrial complexes on the periphery of major cities, has led to increased occupation of soils with poor geotechnical properties, characterized by low strength and high compressibility. To overcome these difficulties, and make possible the construction on such soils, it is common the adoption of reinforcement or stabilization techniques, being the chemical stabilization one of the techniques that have been used with success.

The chemical stabilization of a soil is a technique where the soil is mixed, *in situ,* with cementitious materials in order to improve its mechanical behavior. The result of this mixture are physico-chemical interactions that occur between soil particles, the binders and water present in the soil, resulting in a new composite material with a better mechanical behavior than the original one. This stabilizing effect is consequence of cementitious bonds between soil particles which promote the formation of a new stronger and stiffer matrix.

The chemical stabilization is dependent on a wide range of parameters, being the most important ones associated to the soil properties (particles size and size distribution, plasticity characteristics, organic matter content, chemical composition, pH) and cementitious materials (type, quantity). The inherent characteristics of the soil are in general impossible to change at the site to perform chemical stabilization. So, the subsequent study focus namely on the impact that cementitious materials have on the mechanical behavior of the stabilized soil. The cementitious materials used in practice are, in the majority of cases, Portland cement [1, 2]. However, it is common the replacement of part of the Portland cement by additives [2,3] specifically adapted to the soil requirements, resulting in technical and economic advantages. Among the different types of additives that can be used in chemical stabilization of soils, this work gives special emphasis to additives consisting of extremely fine particles (nanoscale additive), more precisely to carbon nanotubes (CNTs).

Carbon nanotubes (CNTs) are particularly attractive for use in cementitious systems because they appear to be close to ideal reinforcing materials. Their unique physical properties, including ultrahigh specific surface, extremely high yield strength and moduli of elasticity, and elastic behavior all point to the potential of CNTs in reinforcing applications [4]. In addition, the introduction of nanoparticles, which have a fine structure on the order of a few nanometers [5], in the cementitious material, has the potential to affect both the physical structure and the chemical reactions occurring during cement curing. The greatest challenge for the application of carbon nanotubes is associated with its natural tendency to aggregate, resulting in the loss of its beneficial properties. To overcome this problem it is common the use of surfactants (anphiphilic polymers) and/or ultrasonic energy to promote dispersion of carbon nanotubes in suspension. The use of ultrasounds should be minimized because it is an energy-inefficient technique, thus the use of surfactants can help in minimizing ultrasounds requirement.

Most research work to date has been done with carbon nanotubes added to cement pastes and concretes [4,6,7, 8,9] neglecting the study with soil matrixes. The carbon nanotubes are not a cementitious material but once introduced in a soil they are expected to reduce the interparticles' spacing, which will promote the construction of a stronger and stiffer soil skeleton matrix, together with the cementitious materials, therefore improving the mechanical properties of the soil. Thus, optimization of nanoparticles distribution is required (solving problems related with particle agglomeration) to obtain a final material with the best characteristics at a competitive cost.

This work is focused on the application of carbon nanotubes (more precisely, multiwall carbon nanotubes, MWCNTs) on soil stabilization, evaluating its applicability in terms of the quality of the dispersion of the suspension and of the mechanical behavior of the new composite material. For this, a commercial polycarboxylate surfactant (Viscocrete 3008) was characterized and used to disperse the CNTs. The characterization relied on light scattering techniques, including Dynamic and Static Light Scattering and Electrophoretic Light Scattering. Finally, the dispersions of carbon nanotubes were added to the main agent responsible for soil stabilization, the Portland cement, and the mechanical behavior of the stabilized soil was studied by unconfined compressive strength (UCS) tests.

2. Materials and experimental procedure

2.1. Materials

The present work is based on a Portuguese soft soil, taken from a location in the center of Portugal (*Baixo Mondego*) along the side of the A14 motorway. In general, the soil is mostly composed of silt with some clay and sand particles, with a high organic matter content (9.3%), which has a strong influence on some characteristics of the soil, namely, low unit weight (γ = 14.6 kNm^3), high plasticity, high natural water content (w_{nat} = 80.9%), high void ratio, low strength and high compressibility.

The chemical composition of the soft soil (Table 1) reveals a high content of silica (SiO_2) and alumina (Al_2O_3), which confers pozzolanic properties to the soil. Therefore, in the long term it can react with calcium hydroxide producing strength-enhancing reaction products [5, 10]. The soil exhibits a reduced value of pH, which can restrain and/or delay some reactions during the chemical stabilization [2,3,11]. A more detailed description and characterization of the soil can be found in [11,12].

The soil studied was collected to a depth of 2.5 m and was homogenized in laboratory in order to control variations in the main characteristics of the soil, making it easy to have representative samples of the soil in its natural conditions. Once homogenized, the necessary soil for the accomplishment of this work was packaged in a thermo-hygrometric chamber at a temperature of 20 ± 2° C and a relative humidity of 95 ± 5% until the date of use.

Table 1. Chemical properties.

Soil						
CaO *(%)*	**SiO_2** *(%)*	**Al_2O_3** *(%)*	**Fe_2O_3** *(%)*	**MgO** *(%)*	**K_2O** *(%)*	**pH** *(-)*
0.74	62	16	4.8	1.1	3	3.5
Portland cement type I 42.5 R						
CaO *(%)*	**SiO_2** *(%)*	**Al_2O_3** *(%)*	**Fe_2O_3** *(%)*	**MgO** *(%)*	**SO_3** *(%)*	**Cl^-** *(%)*
62.84	19.24	4.93	3.17	2.50	3.35	0.01

The binder selected to chemically stabilize the soil was a Portland cement type I, class of mechanical resistance 42.5 (CEM I 42,5 R), with a chemical composition in terms of the main constituents given in Table 1. The cement particles have a specific surface of 349.0 m^2/kg and are negatively charged (zeta potential measured was -2.14 mV, which is in accordance with [13]). The quantity of Portland cement used for the chemical stabilization of the soil was 175 kilos per cubic meter of soil.

For this exploratory study, it was decided to use MWCNTs mainly due to cost (100€/kg) which is significantly lower than the single-wall carbon nanotubes (SWCNTs). MWCNTs were supplied by Nanocyl and, according to their data, the MWCNT CN7000 have an average diameter of 9.5 nm, average length of 1 500 nm and a specific surface between 250 000 and 300 000 m^2/kg (about 1 000 times higher than cement particles). MWCNTs are composed essentially of pure carbon (90%), with some metal oxides (10%). Further characterization of the MWCNTs was conducted with the assessment of the mass density (1.7 g/cm^3) and zeta potential (-25.2 mV, evaluated by electrophoretic light scattering).

As it was said previously, the surfactants are polymers which have the ability to accumulate on the surface or interface of the MWCNTs, promoting their dispersion in aqueous solutions. In this study it was tested one commercial surfactant in order to promote the dispersion of the MWCNTs. The selected surfactant was Viscocrete 3008 produced by Sika, its composition being undisclosed and protected by legal company rights. This surfactant is a polycarboxylate-based polymer used as superplasticiser on concrete with the main purpose of reducing water needs and increasing its workability. It is known that polycarboxylate polymer acts on the surface of cement particles [15, 16] by surface adsorption and steric effect. Further characterization of the surfactant Viscocrete 3008 was conducted with the assessment of the mass density (1.07 kg/m^3) and viscosity (14.05 mPa.s). Supplementary characterization was made for an aqueous solution with 3% of surfactant (by weight): viscosity (1.84 mPa.s); zeta potential (close to zero evaluated by electrophoretic light scattering); molecular weight (241.5 kDa, evaluated by static light scattering, Fig. 1) and surfactant molecule size (represented by the Z-average diameter, 4.65 nm, evaluated by dynamic light scattering - DLS, Fig. 1).

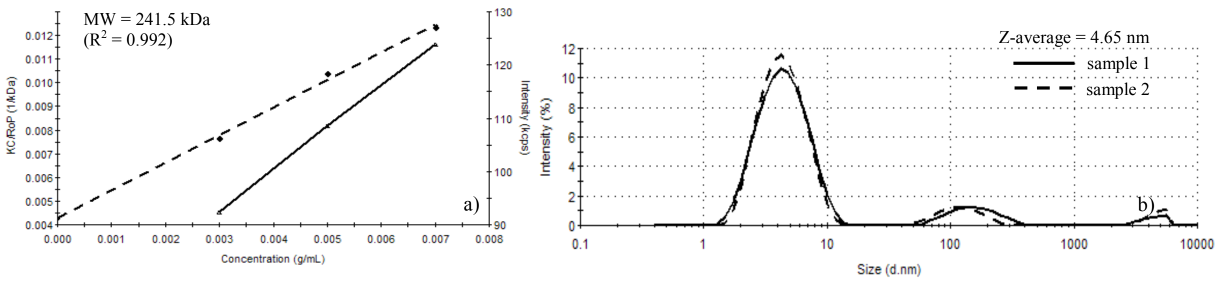

Fig. 1. Aqueous solution with 3% of polycarboxylate: (a) Debye plot for molecular weight; (b) Size distributions by intensity.

2.2. Experimental procedure

The experimental procedure adopted is based in two tests types: size distribution using DLS to assess the quality of the dispersion of MWCNT on an aqueous medium; and unconfined compressive strength (UCS) tests in order to evaluate the mechanical performance of the soil chemically stabilized with a binder which incorporates MWCNT "properly" dispersed in an aqueous medium, either pure water or a solution of polycarboxylate-based surfactant (with a concentration of 3% by weight).

The method tested in this work to demonstrate the applicability of MWCNT dispersions consists in the addition of the MWCNT to an aqueous medium and subsequent application of ultrasonic energy. The tests were made for 3 different quantities of MWCNT: 0.001, 0.01 and 0.1g. The laboratory procedure followed for the evaluation of the dispersions quality was as follows:

1) If surfactant was used water was added in a beaker to the required amount of surfactant to a value not exceeding 200 mL (normally 150 mL) and then shacked for two hours, with the help of a magnetic stirrer, in order to promote a better particle dissolution of surfactant in water, forming the desired solution.
2) The amount of MWCNT was added to a 150 mL beaker with the solution previously prepared.
3) The suspension in the beaker (aqueous solution of surfactant + MWCNT) was subjected to ultrasounds with a power of 500W and during 5 minutes (this was the best compromise power-time obtained from an ultrasonication optimization process, Casaleiro 2014), using a probe-sonicator (Sonics Vibracell 501), with a frequency of 20 kHz. Casaleiro [12] verified that the simple application of ultrasounds increases the temperature of the suspension until 47ºC, promoting undesirable effects in the dispersion of MWCNT. In order to control this temperature rise, an external circuit was set up with coolant water in and out with the permanent addition of crushed ice to guarantee, in this way, that the temperature of the suspension did not exceed 22ºC. Fig.2 presents all the apparatus used during this process, from the ultrasound probe to the cooling circuit with manual addition of crushed ice.
4) The suspension produced was finally analysed by DLS in a ZetaSizer NZS at 25ºC. This step was repeated for all quantities of MWCNT. Two measurements of each suspension were performed.
5) For reference, suspensions of MWCNTs without addition of surfactant and using the same doses of CNTs, were also prepared and characterized by DLS.

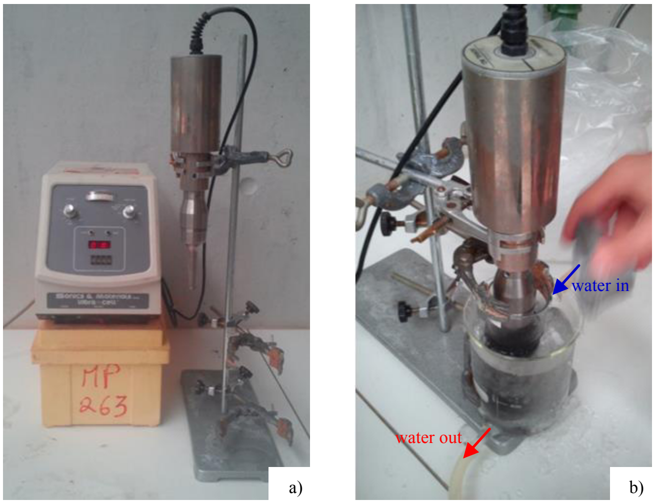

Fig. 2. Apparatus used during the application of ultrasounds to the suspension: (a) sonicator probe Sonics Vibracell 501; (b) cooling circuit.

The second stage of the laboratory work includes performance tests to characterize the mechanical behavior of the soil stabilized with a binder enriched with MWCNT. The experimental procedure involved the following steps (a more detailed description is found in [12,17]):

1) Homogenization of soil: the soil stored was removed from the thermo-hygrometric chamber and was homogenized manually. It was taken the soil mass necessary to prepare two samples. The initial water content of the soil was controlled.
2) Binder preparation: Portland cement was weighed to achieve a concentration of 175 kg of cement by cubic meter of soil.
3) Mixing: the cement was blended in a beaker with 150 mL of suspension (water or aqueous solution of surfactant + MWCNT). Then this mixture was put into the mixing bowl along with soil. It was used a mechanical mixer (Hobart N50) at a rate of 136 rpm. The mixture was homogenized during three minutes. After complete mixing, a small portion of the mixture was withdrawn to assess the water content post-blending. The sample must be introduced in the mold straight away up to a maximum time of 30 minutes after mixing was stopped, otherwise there is a risk of the sample becoming a hard mass.
4) Compression: It was used cylindrical molds made from PVC pipes with inner diameter of 37 mm and height of 325 mm; in the inner surface of the mold, vaseline was smeared in order to promote the sample slide; at the base of the mold it was glued duct tape and a circular geotextile filter so that the sample does not come out of the mold. The samples were introduced in the mold in 6 layers. For each layer, a slight compression was applied with a circular plate followed by application of vibration with the help of a hand drill to eliminate air bubbles within the mixture, followed by new slight compression. This process has always been applied to all 6 layers. In the end a new circular geotextile filter was applied to the top of the sample.
5) Curing: the molds with fresh samples were placed in a vertical position on a curing tank filled with water at a temperature of 20 ± 2°C. During the curing period a vertical pressure of 24 kPa was applied at the top of each sample, in order to simulate actual field vertical effective stress at a depth of 5 m [11]. The curing time for all samples was 7 days.
6) Extraction of sample: after 7 days of sample preparation, the sample was ready to be tested. For that the molds were taken from the curing tank and the samples were demolded using a hydraulic extractor. The specimens were carefully cut so that they had a height of 76 mm and a height/diameter ratio of 2. The specimen was weighed for evaluation of the density.

7) UCS test: the sample is placed on the universal testing machine and subjected to unconfined compression at a constant deformation rate of 1%/min in relation to the height of the sample, which corresponds to 0.76 mm/min. During the test, the force applied to the sample was automatically registered as a function of the displacement of the sample, using a load cell and a displacement transducer, respectively. After reaching rupture, the sample was removed from the test machine and the final water content was measured.

In order to study and characterize the influence of MWCNT dispersions incorporated in the chemical stabilization of the soft soil of *Baixo Mondego*, revealed by its mechanical behavior, a plan of tests was defined as presented in Table2. As it was said previously, two types of tests were made, size distribution by DLS, to characterize the quality of the MWCNT dispersions, and unconfined compressive strength (UCS) tests to evaluate the mechanical performance of the chemical stabilization procedure. A reference test where just water was added to Portland cement was made. As surfactant can promote not only the dispersion of MWCNT but also the dispersion of the particles of soil and cement, tests only with surfactant for a 3% concentration of surfactant were performed as well. Finally, tests with surfactant and MWCNT (applied in different quantities, 0.001, 0.01 and 0.1g) were performed. The nomenclature adopted for the tests is a sum of a letter (W for water only, and PC for an aqueous solution with polycarboxylate surfactant with a concentration of 3%) followed by a number specifying the amount of MWCNT. For each different test conditions, at least two samples were tested. They were only validated if the range of variation of the maximum strength was within the interval defined by the average ± 15%.

Table 2. Test plan.

Solution	MWCNT *(g)*	Test nomenclature	DLS test	UCS test
Water	0	Reference	-	×
	0.001	W0.001	×	×
	0.01	W0.01	×	×
	0.1	W0.1	×	×
Polycarboxylate (3%)	0	PC	-	×
	0.001	PC0.001	×	×
	0.01	PC0.01	×	×
	0.1	PC0.1	×	×

3. Results

Table 3 supplies a summary of all results. The quality of the MWCNT dispersions are expressed by the Z-average value of the dispersed MWCNTs, while the mechanical behavior is characterized by two parameters measured from the stress-strain plots: the maximum unconfined compressive strength ($q_{u\ max}$) and the secant undrained Young's modulus at 50% of the $q_{u\ max}$, E_{u50}.

3.1. Samples without surfactant (water only)

The results regarding the samples prepared only with water are presented in Table 3 and Fig. 3 (for a better understanding of the figure, only one of the samples of each test condition is represented). Fig. 3 presents not only the stress-strain plots obtained from the UCS tests, but also a photography immediately after the ultrasonication process of a suspension of water and MWCNT for the smallest quantity (0.001g). It can be clearly verified at "naked eye" that even for the smallest quantity of MWCNT the dispersion of MWCNT failed, being obvious the presence of aggregates of MWCNT. The principal reason to explain these observations is the lack of surfactant from the solution; the results showed that ultrasonication by itself does not have the ability to disperse the MWCNT particles. Due to this fact, the size distribution by DLS could not be performed for these samples.

Table 3. Summary of results (average values).

Solution	MWCNT *(g)*	Test nomenclature	DLS test	UCS test	
			Z-average *(nm)*	$q_{u\,max}$ *(kPa)*	E_{u50} *(MPa)*
Water	0	Reference	-	117.0	14.4
	0.001	W0.001	(1)	173.1	31.6
	0.01	W0.01	(1)	151.8	28.2
	0.1	W0.1	(1)	169.6	26.4
Polycarboxylate (3%)	0	PC	-	181.4	34.6
	0.001	PC0.001	155.1	190.5	23.8
	0.01	PC0.01	119.5	207.2	30.3
	0.1	PC0.1	139.2	190.3	26.8

(1) Information not available due to the bad dispersion quality verified at "naked eye".

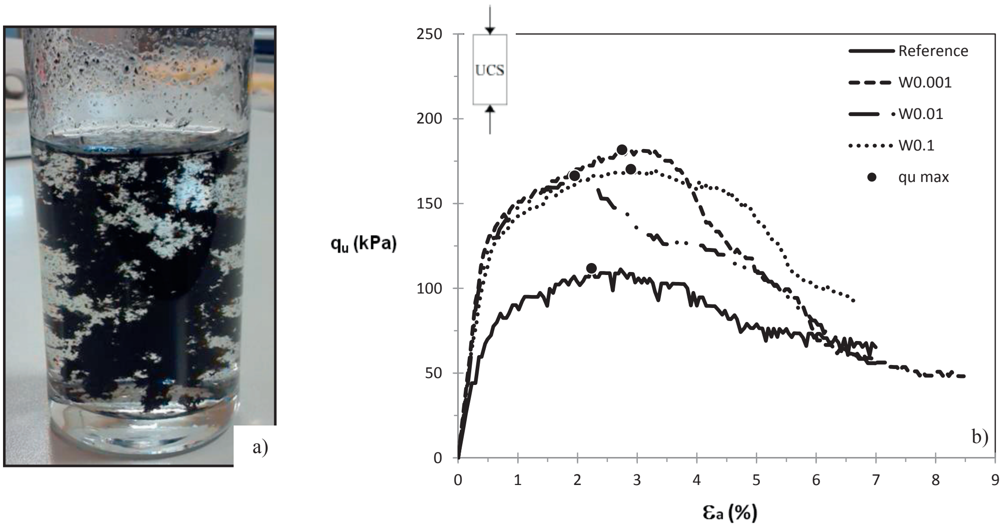

Fig. 3. Laboratory results for samples without surfactant (water only): (a) photograph immediately after ultrasonication of sample W0.001; (b) stress-strain plots (UCS test).

From Table 3 and Fig. 3 it can be seen that, in spite of the bad dispersion of the MWCNT, any incorporation of MWCNT has a beneficial effect in terms of mechanical behavior, since $q_{u\,max}$ and E_{u50} increase when compared with the reference test (stabilized with Portland cement but without MWCNT). The maximum mechanical improvement was obtained for a MWCNT quantity of 0.001g (test W0.001), with an average increment of $q_{u\,max}$ and E_{u50} of 47.9% and 119.4%, respectively (in relation to the reference test). The average results do not present an univocal relation between the quantity of MWCNT and the mechanical parameters, $q_{u\,max}$ and E_{u50}, which may be explained by the fact that the variations observed are within the experimental uncertainty. The results show that even for bad dispersions of MWCNT, the presence of such nanoparticles in the matrix of the stabilized soil has a positive impact in terms of unconfined compression behavior, which is probably explained by the filler effect of such nanoparticles. The results suggest that the improvement can be higher if the quality of MWCNT dispersion increases, since the highest improvement is obtained for the lowest incorporation of MWCNT, which justifies the selection of a surfactant to improve CNT dispersion as shown in the next section.

3.2. Samples with surfactant (polycarboxylate with a concentration of 3% by weight)

The results regarding the samples prepared with an aqueous solution of polycarboxylate with a concentration of 3% by weight are presented in the Table 3 and Fig. 4 (once again, for a better clarity of results, only one of the samples of each test condition is represented in the figure). Fig. 4 presents not only the stress-strain plots obtained from the UCS tests, but also the size distribution of the dispersions obtained by DLS.

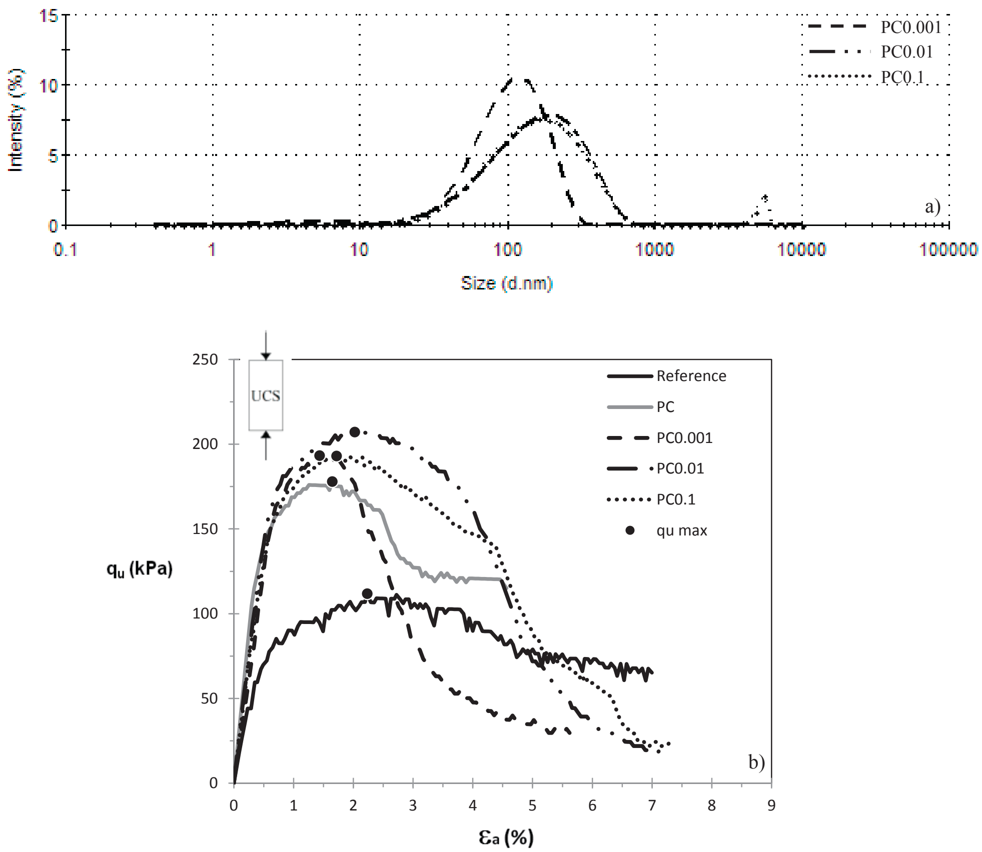

Fig. 4. Laboratory results for samples with surfactant (polycarboxylate): (a) size distribution by intensity (DLS test); (b) stress-strain plots (UCS test).

The analysis of the particle size distributions of the MWCNT dispersed in aqueous solution of polycarboxylate with a concentration of 3% (Table 3 and Fig. 4a) shows that the best dispersion quality was obtained for the sample PC0.001, with a MWCNT quantity of 0.001g. From the analysis of Fig. 4b it can be seen that the best performance in terms of mechanical behavior is associated to the sample with an amount of MWCNT of 0.01g. This corresponds to the maximum amount of MWCNT that could be dispersed in the soil without forming a significant number of aggregates (the difference in the size distribution between samples PC0.001 and PC0.01 is not very substantial). In relation to the reference test, the average increment of $q_{u\,max}$ and E_{u50} was 77.1% and 110.4%, respectively.

As the quantity of MWCNT increases from 0.001 to 0.01g, the mechanical behavior improves as expressed by the parameters $q_{u\,max}$ and E_{u50}. For a further increment, to 0.1g, the mechanical behavior decreases which may be due to the high number of nanoparticles for the concentration of surfactant used (a higher concentration of surfactant should be tested). Notice that for this last MWCNT sample (PC0.1), the particle size distribution (Figure 4a) presents a second peak/mode expressing the existence of aggregates, which seems to be co-related to the UCS results.

From comparing the results of the samples with and without surfactant it can be seen clearly the importance of the presence of the surfactant polycarboxylate, which has a positive impact in terms of mechanical behavior due to the best quality of the dispersions of MWCNT.

As stated in section 2.1, the polycarboxylate-based surfactant acts not only on the surface of MWCNT particles but also on the surface of cement particles. Thus, it is expected a better mechanical performance due to the presence of such polymer on the stabilization of the soil, associated to a better dispersion of the cement particles trough the stabilized soil matrix. This expected result was proven with the test PC (soil stabilized with Portland cement and an aqueous solution with polycarboxylate at a concentration of 3% by weight) which presented better mechanical properties than the reference test.

The combination of the effects associated to the incorporation of MWCNT with the presence of surfactant is not a superposition of effects (direct sum) as stated in Table 3 and Figures 3 and 4, due to the interdependence between both effects.

The surfactant used in these tests is a non-ionic polymer acting according to the steric mechanism, which is very much dependent on the surfactant concentration. Thus, testing a range of surfactant concentrations will be very important to optimize its action.

4. Conclusions

The results presented are part of a preliminary study about the benefits of the introduction of nanoparticles in a soil chemically stabilized with Portland cement. The results have shown that the presence of nanoparticles in a soil-cement matrix has the ability to reduce the interparticles' spacing, which will promote the construction of a stronger and stiffer soil skeleton matrix together with the cementitious materials, therefore improving the mechanical properties of the material. The mechanical enhancement can be increased if the quality of the MWCNT dispersion improves, which can be obtained by adding a polycarboxylate-based polymer to the solution. Finally, it was shown that the addition of even a very small quantity of MWCNT, effectively dispersed, improves the mechanical properties of a soil chemically stabilized with cement, this improvement reaching values of the order of 77.1% and 110.4%, respectively for the $q_{u\,max}$ and E_{u50}.

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References

[1] A. Porbaha,., State of the art in deep mixing technology: part I. Basic concepts and overview, Ground Improvement, 2 (1998) 81–92.
[2] M. Kitazume, M. Terashi, The deep mixing method – principle, design and construction, edited by Coastal Development Institute of Technology, Japan, Balkema, 2002.
[3] T. B. Edil, D. A. Staab, Practitioner's guide for deep-mixed stabilization of organic soils and peat, Final Report, The National Deep Mixing Research Program, Project Number NDM302, 2005.
[4] J. M. Makar, The Effect of SWCNT and Other Nanomaterials on Cement Hydration and Reinforcement, in: K. Gopalakrishnan, B. Birgisson, P. Taylor, N. O. Attoh-Okine (Eds.), Nanotechnology in Civil Infrastructure, 103-130, 2011.
[5] H. F. W. Taylor, Cement Chemistry, 2nd edition, Thomas Telford, 1997.
[6] J. M. Makar, G. W. Chan, Growth of cement hydration products on single-walled carbon nanotubes, Journal of the American Ceramic Society 92, 6 (2009) 1303–1310.
[7] L. Raki, J. Beaudoin, R. Alizadeh, J. Makar, T. Sato, Cement and Concrete Nanoscience and Nanotechnology, Materials 3, (2010) 918-942.
[8] A. Cwirzen, K. Habermehl-Cwirzen, V. Penttala, Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites, Advances in Cement Research 20, 2 (2008) 65-73.
[9]M. S. Konsta-Gdoutos, Z. S. Metaxa, S. P. Shah, Highly dispersed carbon nanotube reinforced cement based materials, Cement Concrete Res., 40 (2010) 1052–1059.
[10] M. Janz, S. E. Johansson, The function of different binding agents in deep stabilization, Swedish Deep Stabilization Research Centre, Report 9, Linköping, Sweden, 2002.

[11] A. A. S. Correia, Applicability of deep mixing technique to the soft soil of Baixo Mondego, Ph.D. dissertation, Univ. of Coimbra, Coimbra, Portugal, 2011. (in Portuguese)
[12] P. D. F. Casaleiro, Chemical stabilization of the soft soil of Baixo Mondego by nanomaterials, MSc. Thesis, Univ. of Coimbra, Coimbra, Portugal, 2014. (in Portuguese)
[13] S. Srinivasan, S. A. Barbhuiya, D. Charan, S. P. Pandey, Characterising cement–superplasticiser interaction using zeta potential measurements, Construction and Building Materials 24(12) (2010) 2517-2521.
[14]B. J. Elliott, M. Gilmore, Fiber Optic Cabling, Newnes, 2nd edition, 2002.
[15] F. Puertas, H. Santos, M. Palacios, S. Martínez-Ramírez, Polycarboxylate superplasticiser admixtures: effect on hydration, microstructure and rheological behaviour in cement pastes, Advances in Cement Research 17, 2, (2005) 77–89.
[16] S. A. G. B. P. Coelho, Estudo das propriedades dos adjuvantes na compatibilidade/robustez cimento/adjuvante. MSc. Thesis, Higher Institute of Engineering of Lisbon, 2012. (in Portuguese)
[17] A. A. S. Correia, P. D. F. Casaleiro, M. G. Rasteiro, Chemical stabilization of soft soil of Baixo Mondego with nanomaterials, 14th National Geotechnical Conference, Covilhã, Portugal, 2014.