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Surfactants for dispersion of carbon nanotubes applied in soil stabilization

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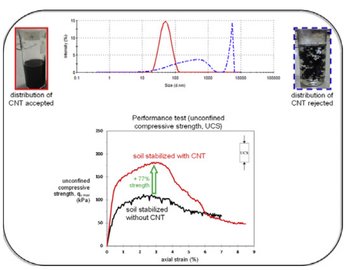
GRAPHICAL ABSTRACT



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ABSTRACT

The discovery of the unique properties of carbon nanotubes (CNT) did grow interest to its application in nanocomposites, for a wide variety of purposes. However, the greatest challenge for its application is associated with the natural tendency to aggregate, resulting in the loss of its beneficial properties. To overcome this problem it is common the use of surfactants and/or ultrasonic energy to promote their dispersion in suspension. This work is focused on the influence of surfactants' properties on the dispersion of carbon nanotubes and on the influence of the quality of the dispersions on the mechanical properties of stabilized soil. Two surfactants (Glycerox and Amber 4001 differing in molecular weight and charge) were fully characterized, followed by the study of which surfactant concentrations were more efficient on the dispersion of the CNTs. The characterization methods were based on light scattering techniques: Dynamic Light Scattering (DLS) for the hydrodynamic diameter and Static Light Scattering (SLS) for the molecular weight. Suspensions of CNTs were prepared in solutions of the aforementioned surfactants, with different concentrations, and further dispersion was promoted using ultra-sounds (20 kHz during 5 min). The dispersions of CNTs in these two surfactants were then fully characterized using again DLS. Finally, the dispersions of carbon nanotubes were added to the main agent responsible for soil stabilization, the binder (Portland cement type I 42.5R), and the mechanical behavior of the new composite material was studied by unconfined compression strength (UCS) tests. The results of the UCS tests led to conclude that the introduction of CNTs in the binder can have huge impact on the mechanical properties of the stabilized soil. Furthermore, the quality of the dispersion of CNTs has got a very high impact on the performance achieved. It was verified an improvement up to 77% on the compressive strength of the material and 155% on Young's modulus, referred to the reference test where no carbon nanotubes nor surfactant were added, fundamentally dependent on surfactant type and concentration used.

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1. Introduction

The sudden growth of urban perimeter due to 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. As a result of this mixture there 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 a 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 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 tune the chemical stabilization. So, the subsequent study focus on the impact that cementitious materials, in the majority of cases Portland cement [1,2], have on the mechanical behavior of the stabilized soil and on the possibility of replacing part of the Portland cement by additives [2,3] specifically adapted to the soil requirements, resulting in technical and economic advantages. In this exploratory work it is studied a nanoparticle-based additive, more precisely carbon nanotubes (CNTs).

Carbon nanotubes (CNTs) are particularly attractive for use in cementitious systems because they are 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 as an additive in soil stabilization 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 [4,6–9] 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. Two surfactants (Glycerox and Amber 4001 – different molecular weight and charge) were chosen for this purpose. The choice was to evaluate the influence of molecular weight and charge on the quality of the dispersion. The two surfactants were fully characterized before being used to disperse the CNTs. Then, the characterization of the dispersions of CNTs in these surfactants solutions was performed. 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 (region known as *Baixo Mondego*). In general, the soil is mostly composed of silt (2 μm < size < 0.6 mm: 66%) with some clay (size < 2 μm: 12%) and sand (0.6 mm < size < 2 mm: 22%) particles, with a high organic matter content (9.3% w/w), which has a strong influence on some characteristics of the soil, namely, low unit weight (γ = 14.6 kN/m^3), high plasticity, high natural water content (w_{nat} = 80.9% w/w), high void ratio, low strength and high compressibility. Moreover, the soil exhibits a specific gravity of 2.555 and a porosity of 67.8%.

The analysis of the mineralogical and chemical composition of the soft soil (Table 1) reveals a high content of silica (SiO_2) and alumina (Al_2O_3), which combined with its fineness 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 [11–13].

The soil studied was collected at 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.

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 2. The cement particles have a specific surface of 349.0 m^2/kg and are negatively charged (zeta potential measured using electrophoretic light scattering – Zetasizer NanoZS from Malvern Inst., UK, was −2.14 mV, which is in accordance with [14]). The amount 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 producer data, the MWCNT CN7000 have an average diameter of 9.5 nm, average length of 1500 nm and a specific surface between 250,000 and 300,000 m^2/kg (about 1000 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

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