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Chemical stabilization of soils using carbon nanotubes

Master's thesis in the scientific area of Chemical Engineering, supervised by Professor Doctor Maria da Graça Bomtempo Vaz Rasteiro and Professor Doctor António Alberto Santos Correia and submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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"Be the change that you wish to see in the world."

Mahatma Gandhi

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Abstract

The recent demand for construction on soils with poor geotechnical characteristics (such as soft soils) has led to a rising need to seek new and better methods of soil stabilization. The work developed in this dissertation focused on the study of the mechanical properties of the soft soil of *Baixo Mondego*, after its chemical stabilization with Portland cement and enriched with carbon nanotubes.

Since their discovery, carbon nanotubes have found a wide variety of applications due to their exceptional properties, most of which consisting on their incorporation into composite materials to act as a nanoreinforcement agent. However, the natural tendency for the aggregation of these nanoparticles may lead to the loss of their beneficial properties, hence it is necessary to guarantee a suitable dispersion before their use. This can be achieved by adding surfactant molecules and/or applying ultrasonic energy to promote a stable dispersion of such particles.

In this study, seven surfactants (Amber 2009, Amber 2012, Amber 2013, Amber 2014, polyDADMAC HMW, polyDADMAC MMW and Pluronic F-127) and two surfactant mixtures (Pluronic F-127 with polyDADMAC MMW and Glycerox with polyDADMAC MMW) were characterized and tested to evaluate their efficiency in dispersing multi-wall carbon nanotubes (MWCNTs). All surfactants proved to be capable of promoting a suitable dispersion of 0.001 wt.% MWCNTs when used at a concentration of 0.1 wt.%.

Subsequently, the well-dispersed MWCNTs were added to the soft soil of *Baixo Mondego* and Portland cement, and unconfined compression strength tests (UCS) were carried out in order to assess the mechanical behaviour of the final composite material. The results showed that all composite samples exhibit a more ductile behaviour than the reference test. Regarding the mechanical compression strength, the improvements observed were relatively poor, and in some cases there was even a loss of the unconfined compression strength, which is most likely due to the surfactant behaviour when placed in the soil medium, before the cement hydration reactions start occurring.

In the end, it was concluded that further studies are necessary to better understand the interactions between the surfactant/MWCNTs system when added to the soil/Portland cement composite, since having a good dispersion of MWCNTs was not enough to obtain reasonable mechanical improvements of the final composite materials, as initially expected.

Keywords: Carbon nanotubes; Nanocomposites; Dispersion; Surfactants; Soil stabilization.

Resumo

A recente necessidade de construção em solos com fracas características geotécnicas (como é o caso dos solos moles) tem conduzido a uma crescente procura de novos métodos de estabilização de solos. O trabalho desenvolvido no âmbito desta dissertação focou-se no estudo das propriedades mecânicas do solo mole do Baixo Mondego, após a sua estabilização química com cimento Portland e com nanotubos de carbono.

Desde a sua descoberta, os nanotubos de carbono têm encontrado inúmeras aplicações devido às suas propriedades excepcionais, muitas das quais consistem na sua incorporação em materiais compósitos, para atuarem como agentes de reforço à nanoescala. No entanto, a tendência natural que estas partículas têm para a sua aglomeração pode levar à perda das suas propriedades benéficas, e por isso é necessário garantir uma dispersão adequada antes do seu uso. Através da adição de surfactantes e/ou aplicando energia ultrassónica é possível promover uma dispersão estável destas partículas.

Neste estudo, foram caracterizados e testados sete surfactantes (Amber 2009, Amber 2012, Amber 2013, Amber 2014, polyDADMAC HMW, polyDADMAC MMW e Pluronic F-127) e duas misturas de surfactantes (Pluronic F-127 com polyDADMAC MMW e Glycerox com polyDADMAC MMW), de forma a avaliar a sua eficiência na dispersão de nanotubos de carbono de parede múltipla (MWCNTs - *multi-wall carbon nanotubes*). Todos os surfactantes foram capazes de promover uma dispersão adequada de 0.001 wt.% de MWCNTs, quando usados numa concentração de 0.1 wt.%.

Subsequentemente, os MWCNTs dispersos foram adicionados ao solo mole do Baixo Mondego e a cimento Portland, e foram realizados ensaios de compressão simples (UCS - *unconfined compression strength*) de forma a avaliar o comportamento mecânico do material compósito final. Os resultados mostraram que todas as amostras exibem um comportamento mais dúctil do que os ensaios de referência. Relativamente à resistência mecânica, não foram registadas melhorias significativas, e em alguns casos houve até uma diminuição da resistência das amostras à compressão não confinada, o que provavelmente se deve ao comportamento do surfactante quando em contacto com o solo, antes de terem lugar as reações de hidratação do cimento.

À luz dos resultados obtidos, conclui-se que é necessário efetuar estudos adicionais para compreender melhor as interações entre o sistema surfactante/MWCNTs quando este é adicionado ao compósito solo/cimento Portland, uma vez que ter uma boa dispersão de MWCNTs não é suficiente para assegurar melhorias ao nível das propriedades mecânicas dos materiais compósitos finais, como seria esperado.

Palavras-chave: Nanotubos de carbono; Nanocompósitos; Dispersão; Surfactantes Estabilização de solos.

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Nomenclature

$\Delta\delta_v$	Variation of the Axial Deformation
δ_v	Vertical Displacement
λ_o	Laser Wavelength
μ	Dynamic Viscosity
ε	Vertical Strain
-COOH	Carboxyl group
-OH	Hydroxyl group
A₂	2 nd Virial Coefficient
A_c	Corrected Cross-Sectional Area
Al₂O₃	Aluminum Oxide
CaO	Calcium Oxide
CCF	Carboxylated Carbonaceous Fragments
CCVD	Catalytic Chemical Vapor Deposition Process
CEM I 42.5 R	Portland Cement Type I Class of Mechanical Resistance 42.5
CMC	Critical Micelle Concentration
CNT	Carbon Nanotube
CTAB	Cetyl Trimethyl Ammonium Bromide
D_c	Translational diffusion coefficient
D_h	Hydrodynamic Diameter
D_i	Hydrodynamic Diameter of Class i
D_z	Average Diameter of the Size Distribution
DLS	Dynamic Light Scattering
DMF	Dimethyl Formamide

dn/dc	Differential Refractive Index Increment
DTAB	Dodecyl Trimethyl Ammonium Bromide
ELS	Electrophoretic Light Scattering
Eu₅₀	Secant Undrained Young's Modulus
Fe₂O₃	Iron Oxide (III)
F	Force
H₂SO₄	Sulphuric Acid
HMW	High Molecular Weight
HNO₃	Nitric Acid
I_A	Residual Scattering Intensity of the Analyte
I_i	Scattered Light Intensity of Class i
I_T	Toluene Scattering Intensity
K	Optical Constant
k	Boltzmann Constant
LDV	Laser Doppler Velocimetry
MgO	Magnesium Oxide
MMW	Medium Molecular Weight
MWCNT	Multi-Wall Carbon Nanotube
MW	Molecular Weight
N_A	Avogadro's Constant
n_o	Solvent Refractive Index
n_T	Toluene Refractive Index
NaCl	Sodium Chloride
P_θ	Angular Dependence of the Scattering Intensity
polyDADMAC	PolyDiallyl Dimethyl Ammonium Chloride

PVA	Poly Vinyl Alcohol
PVC	Poly Vinyl Chloride
PVP	Poly Vinyl Pyrrolidone
q_{umax}	Maximum Unconfined Compressive Strength
q_u	Unconfined Compressive Strength
R_θ	Rayleigh Ratio
R_T	Rayleigh Ratio of Toluene
RI	Refractive Index
SDBS	Sodium Dodecyl Benzene Sulfonate
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscopy
SiO₂	Silicon Dioxide
SLS	Static Light Scattering
SO₃	Sulfur Trioxide
SOCT	Sodium Octanoate
SWCNT	Single-Wall Carbon Nanotube
TEM	Transmission Electron Microscopy
T	Absolute Temperature
U_E	Electrophoretic Mobility
UCS	Unconfined Compression Strenght
W_f	Final Water Content
ZNS	Zetasizer Nano Series
Z	Zeta Potential

Chapter 1

Introduction

Over the last century, there has been both an economical and demographic growth worldwide which has inevitably lead to an exhaustion of the land sources with appropriate geotechnical properties for construction works, mainly around metropolitan areas. Thus, there has been a big pressure to construct on soils with poor geotechnical characteristics (such as soft soil). These soils by its own are unsuitable for construction due mainly to their low strength and high deformability. In order to overcome this problem, several methods of ground improvement can be carried out, including chemical stabilization, which will be the focus of this work.

The chemical stabilization process consists on the addition of components to a soil, which will aid to bind the soil particles together improving its mechanical properties. The most used binder agent is the Portland cement, which can be used along with other additives. The chemical stabilization of a soil depends on several factors, which should be further studied to achieve a better enhancement of its mechanical strength, given the structural requirements needed and the variability inherent to the natural material, soil.

In this context, the aim of this work is to study the chemical stabilization of the soft soil of *Baixo Mondego*, with the addition of Portland cement enriched with carbon nanotubes, and its influence on the mechanical properties of the final composite material.

Even though the discovery of carbon nanotubes (CNTs) was somewhat recent, during the last two decades these materials have become a subject of great importance, both at the academic and, more recently, at the commercial level. Their outstanding mechanical, electrical, thermal and optical properties allow the CNTs to be employed in a vast number of applications, most of which are based on the development of reinforced composite materials.

One of the most recent fields of application studied is its incorporation in the soil, along with Portland cement, to improve its mechanical properties. The presence of such small particles in the soil/cement matrix is beneficial, since these particles can, on one hand, occupy the empty spaces in the matrix (acting as nanofillers), and on the other hand contribute to the formation of cementitious bonds between the soil particles, therefore promoting the formation of a stronger and stiffer matrix (acting as nanoreinforcements).

However, due to their nanoscale, hydrophobic nature and strong Van der Waals forces, carbon nanotubes are quite difficult to disperse in a solution and their natural tendency is towards agglomeration, with the formation of bundles. In this scenario, most of the beneficial properties of these nanomaterials are lost, and its addition into composite ma-

materials results in no major benefit for the final product. Taking into account the cost of these materials, it is crucial to address this problem before proceeding with the rest of the work.

A good dispersion of CNTs can be achieved through several methods. Among them, a combination of two methods was chosen for this work by using ultrasounds, which is a mechanical method, and adding surfactants, which is a chemical method.

The work plan for this research was as follows - first, all surfactants were characterized before use, including the ones tailored specifically for this work provided by aquaTECH (Amber 2009, Amber 2012, Amber 2013, Amber 2014) and commercial ones acquired from aquaTECH (Glycerox) and from Sigma-Aldrich (polyDADMAC HMW, polyDADMAC MMW and Pluronic F-127). Then, the concentration of surfactant that could better disperse the CNTs was optimized. This suspension was then mixed with Portland cement producing a slurry, which was added to the soil. At the end unconfined compression strength tests (UCS) were performed to assess the mechanical behaviour of the final composite material.

This dissertation is structured in the following five chapters:

- Chapter 1, the introduction, where the motivation and objectives of this work are summarized;
- Chapter 2, the state of the art, where the fundamental theoretical concepts of this research are explained, and the results of previous works in this field are presented;
- Chapter 3, where the information on the characterization of the materials used, as well as the experimental methodology followed to evaluate the mechanical strength of the soil, is presented;
- Chapter 4, where the results obtained from this study are presented and subjected to a critical analysis;
- Chapter 5, where the main conclusions drawn from this work are stated, and future works are proposed.

Chapter 2

State of the art

2.1 Carbon nanotubes (CNTs)

The first report presented to the scientific community on carbon nanotubes (CNTs) was published by Sumio Iijima, in 1991. In his paper, Iijima reported the synthesis and observation of tubular structures made entirely of carbon atoms, bonded in a hexagonal lattice, and composed of concentric layers (ranging from 2 to 50). Their length was in the micrometer range; however, their diameter varied between 4 and 30 nanometers, which lead to the designation of carbon nanotubes [1].

The discovery of CNTs was the first step to a major breakthrough in the field of nanotechnology. From this point forward, these materials have attracted a great deal of attention, owed to the remarkable properties that they revealed, which impart them with an enormous versatility of applications in which they can be employed. This growing interest is clearly evidenced by the sudden increase in both the number of publications and patents regarding this subject over the last decades. Furthermore, many efforts have been employed to find a suitable way to increase CNTs production capacity, at lower costs, in order to enable its use in commercial applications [2, 3].

2.1.1 Classification and properties

Classification of CNTs

Carbon is one of the most versatile elements known, with the ability to form different materials with very distinct characteristics, according to its hybridization state and the spacial arrangement of its atoms. Carbon nanotubes are amongst such allotropes [4]. Perhaps the simpler way to understand what are carbon nanotubes is to described them as a graphene sheet, folded into a cylindrical tube, as it is represented in Figure 2.1 [5].

According to the number of concentric tubes that compose their structure, CNTs can be classified as single-wall carbon nanotubes (SWCNTs) or as multi-wall carbon nanotubes (MWCNTs). The former comprises only one graphene sheet wrapped into a tubular structure, while the latter contains several graphene sheets wrapped concentrically around each other, as it is shown in Figure 2.2. As expected, this induces a substantial difference in CNTs diameter and structure, and in its properties as well. The diameter of SWCNTs usually ranges from 0.8 to 2 nm while MWCNTs normally present diameters ranging from 5 to 20 nm, although this value can reach 100 nm [2, 6]. Their length,

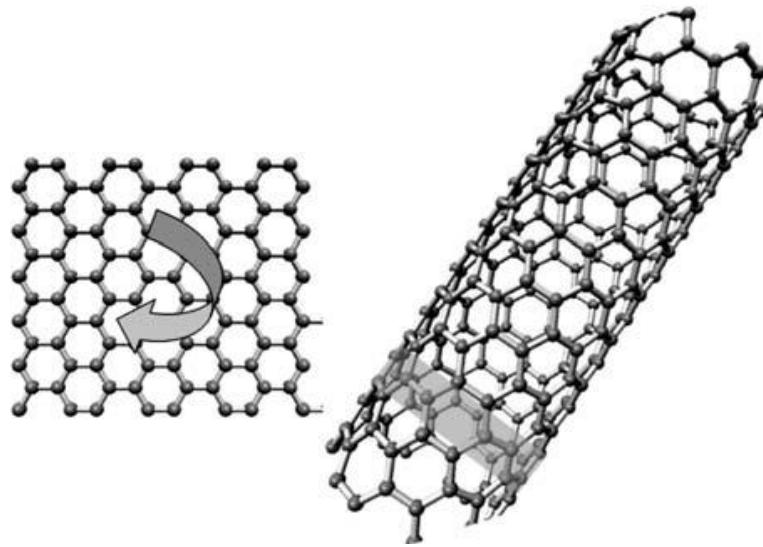


Figure 2.1: Graphene sheet folded into a carbon nanotube [5].

however, can extend to the micrometre scale, giving rise to one of the most distinguishing characteristics of these materials - their high aspect ratio (length/diameter), which is generally higher than 100, and high surface area [5, 7].

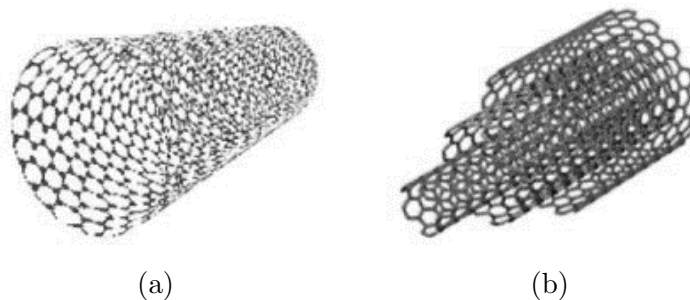


Figure 2.2: a) Single-wall carbon nanotubes; b) multi-wall carbon nanotubes [8].

The CNTs may also be classified according to their chirality, i.e., the orientation of its hexagonal-latticed walls with respect to the tube axis. Taking into account this parameter, the CNTs structure can be of three types - armchair (Figure 2.3a), zig-zag (Figure 2.3b) and chiral (Figure 2.3c). The chirality, as well as the diameter, have a significant impact on CNTs electric properties, defining its conducting behaviour as metallic or semi-conducting [5, 7].

Properties of CNTs

Carbon nanotubes have been labelled as one of the most promising materials of modern science, exhibiting extraordinary properties which arise from the sp^2 hybridization of their carbon-carbon bonds. As mentioned previously, the wall structure of CNTs is composed of a hexagonal shaped network, in which each carbon atom is bonded to three more carbon

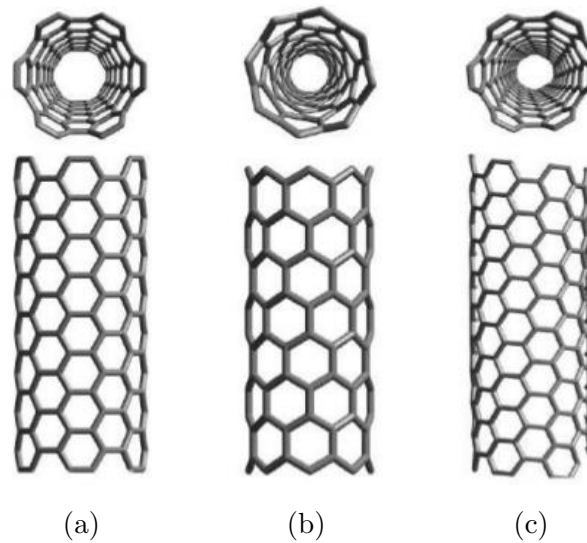


Figure 2.3: Classification of carbon nanotubes according to their chirality [9]: a) armchair; b) zigzag; c) chiral.

atoms. This linkage configuration is possible because these atoms contain sp^2 hybridized orbitals, which means that each carbon atom contains three sp^2 orbitals that will each overlap with another sp^2 orbital of another carbon atom, thus allowing their covalent bonding to each other in this particular arrangement [10, 11].

The mechanical and physical properties of CNTs are considerably better than traditional materials such as steel. Although these values may differ according to the structure and properties of the CNTs under study, the Young's modulus measured for CNTs is around 1 TPa, and values of tensile strength above 100 GPa have been recorded [2, 7, 12]. Furthermore, they are very flexible and their specific gravity is around 1800 kg/m^3 , meaning that CNTs are also light materials, which combined with the mechanical properties described above can be very useful for a wide variety of applications [7]. When compared to steel, CNTs have a modulus of elasticity roughly five times higher, a tensile strength nearly 100 times stronger and elastic strain capacities 50 times greater, with a specific gravity one-sixth of steel [13].

As said previously, CNTs can be either metallic or semi-conducting, depending on their dimensions and chirality. Nonetheless, it is proven that they have low electrical resistance (due to their morphology, which leads to lower scattering effects), and they are able to carry current densities as high as 10^9 A cm^{-2} [2, 12], making them one of the most interesting materials to enhance the conductivity of nanocomposites. One of the most important emerging fields in this area is the development of conductive polymer nanocomposites, with many reports found in the literature over the last years [12, 14, 15].

Regarding their thermal properties, CNTs have surpassed diamonds as the best thermal conductor known, with SWCNTs having a thermal conductivity that can reach values

around $3500 \text{ W m}^{-1} \text{ K}^{-1}$ [2, 12].

It is however important to realize that these properties are highly dependent on both the CNTs morphology and purity, and since to date there is no synthesis process capable of yielding uniform batches of CNTs, the values referred above may vary slightly, according to the type of CNTs used and its dispersion state [7].

2.1.2 Dispersion of CNTs

The most problematic aspect of CNTs in terms of workability is their inherent insolubility in most solvents, both aqueous and organic [5, 7]. The hydrophobic nature of CNTs, along with the strong Van der Waals forces acting on them, leads to a high tendency for aggregation, forming bundles [16]. These effects are a consequence of the large surface area and high aspect ratio of these materials, which favour their agglomeration [7].

In order to maximize the benefits of adding CNTs to composite materials, it is crucial to overcome the problems related to particle agglomeration. Thus, it is necessary to employ certain techniques in order to obtain a good and homogeneous dispersion of CNTs, so as not to lose their beneficial properties. The methods used to improve the CNTs dispersion in a solvent can be either chemical or mechanical [7]. These methods will be described in further detail in the next sections.

2.1.3 Chemical dispersion of CNTs

The chemical dispersion of CNTs involves two main approaches, covalent and non-covalent functionalization, both of which induce modifications on the CNTs surface.

Covalent functionalization

This method consists on the covalent attachment of functional groups onto the CNTs surface, which will improve their solubility in a solvent. For instance, to enhance their dispersion in an aqueous solvent, polar groups (such as -OH and -COOH) are added to increase their wettability [17].

The bonding of functional entities can be achieved through direct covalent functionalization of the CNTs sidewalls, which implies a change of some of the carbon atoms' hybridization from the sp^2 to the sp^3 state, therefore losing some of their properties [7, 16].

However, the linkage of these groups is more likely to occur at defect sites, since they are more reactive. Therefore, covalent functionalization can also be conducted by grafting functional groups at the existing defect sites on CNTs, or by acid functionalization, which includes a pre-treatment of the CNTs with strong acids, with the purpose of creating

defect sites through oxidation, so that the desired functional groups can be linked to the CNTs' wall [5, 7]. For this procedure, it is typical to use nitric acid (HNO_3) to oxidize the surface of the CNTs, and then adding sulphuric acid (H_2SO_4) to roughen the surface, creating topological defects [18].

One of the biggest benefits of applying this technique is that it allows the tuning of the CNTs structure (and consequently, their behaviour) for certain applications. For instance, significant improvements on mechanical strength of CNTs-polymer nanocomposites have been reported when the CNTs incorporated were grafted with polymer molecules on these active functional sites [15].

Even though this method can attain quite good dispersions of CNTs, for some applications its disadvantages outweigh its advantages. The covalent bonding of functional groups inevitably introduces more defect sites to the CNTs structure, through which fracture may occur, decreasing their beneficial properties [16]. Furthermore, the disruption of the CNTs structural network is very likely to have a negative impact on the properties of the final composite materials [5].

During acid functionalization, several by-products composed of condensed aromatic graphitic rings with various functional groups attached (also known as carboxylated carbonaceous fragments, or CCFs) are generated. For applications within the scope of this work, such as the addition of CNTs in cementitious materials, these fragments can hinder the improvement of the mechanical properties of the final composite material by reacting with the Portland cement, thus preventing the CNTs from taking part in these reactions and acting as a nanoreinforcement agent [19].

Non-covalent functionalization

A promising method included in the field of chemical dispersion of CNTs is the non-covalent functionalization. In this case, several types of molecules (for example polymers, surfactants and biomolecules, among others) are used to adsorb onto the nanotube surface and reduce the interfacial energy between the CNTs sidewalls and the solvent [7]. The electrostatic or steric repulsion (depending on whether the molecules are charged or not) keeps the nanotubes apart from each other, counteracting the Van der Waals attraction forces [7].

To date, many surfactants and polymers have been explored to this end, since this is a technique with great potential. More recently studies have also focused on the mixing of different surfactants, in order to assess if there are synergistic effects that may further enhance CNTs dispersion [20].

Kaur et al. [21] conducted a study on the interactions between polydiallyl dimethyl ammonium chloride (polyDADMAC) and MWCNTs in the presence of different sur-

factants, assessing the influence on their dispersion action. To this end, the MWCNTs/polyDADMAC system was combined with a series of surfactants of different ionic nature (cationic, anionic and non-ionic). The authors verified that a good dispersion of MWCNTs only occurred for the combination of MWCNTs/polyDADMAC and three of the non-ionic surfactants used (namely Tween 20, Tween 80 and Triton X-100); the system containing Triton X-100 exhibited the best performance, which was attributed to π - π interactions between the benzene ring of Triton X-100 and the hexagonal rings of carbon atoms on the graphitic surface of MWCNTs¹. In Figure 2.4 it is clear that MWCNTs with polyDADMAC and Triton X-100 (Figure 2.4b) are much less aggregated than the MWCNTs (Figure 2.4a). Furthermore, an analysis on the amount of defects was carried out and revealed that the non-covalent functionalization of polyDADMAC on MWCNTs is less destructive when compared to their covalent functionalization using strong acids and bases, which creates more defect sites.

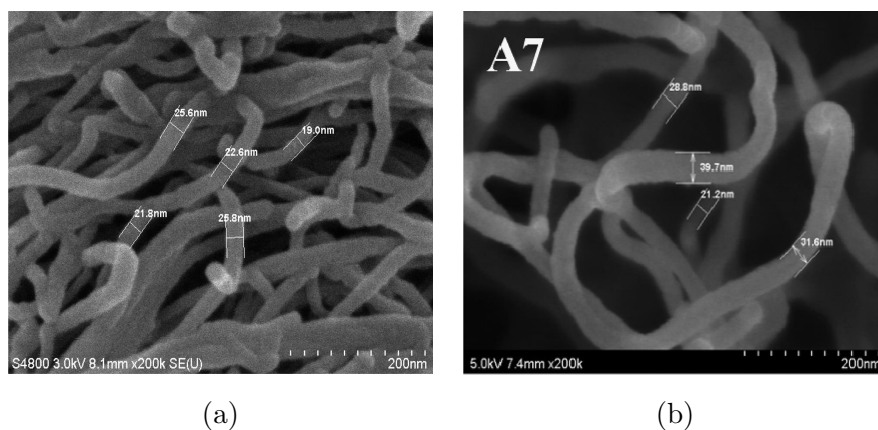


Figure 2.4: SEM (Scanning Electron Microscopy) micrographs of: a) MWCNTs; b) MWCNT/polyDADMAC system in the presence of Triton X-100 [21].

Madni et al. [22] studied the dispersion efficiency of MWCNTs with mixtures of a cationic and an anionic surfactant, namely dodecyl trimethylammonium bromide (DTAB) and sodium octanoate (SOCT). Several surfactant concentrations were tested (with a constant ratio of 1:1 of DTAB/SOCT), using dimethyl formamide (DMF) as solvent and subjecting the samples to 2 hours of ultrasonication. TEM measurements (Transmission Electron Microscopy) revealed that the mixed surfactant system promotes a better dispersion of MWCNTs at lower concentrations than each of these surfactants alone. In Figure 2.5 the uniform coating of MWCNTs by the surfactants mixture is evident. This

¹The carbon atoms that constitute the benzene ring present in Triton X-100 have sp^2 hybrid orbitals, exactly like the carbon atoms in CNTs. This means that in both structures a p orbital remains unhybridized, and when these structures come into contact with one another, these orbitals can interact with each other by π - π interactions.

provides an effective steric barrier against agglomeration, keeping this dispersions stable over long periods of time.

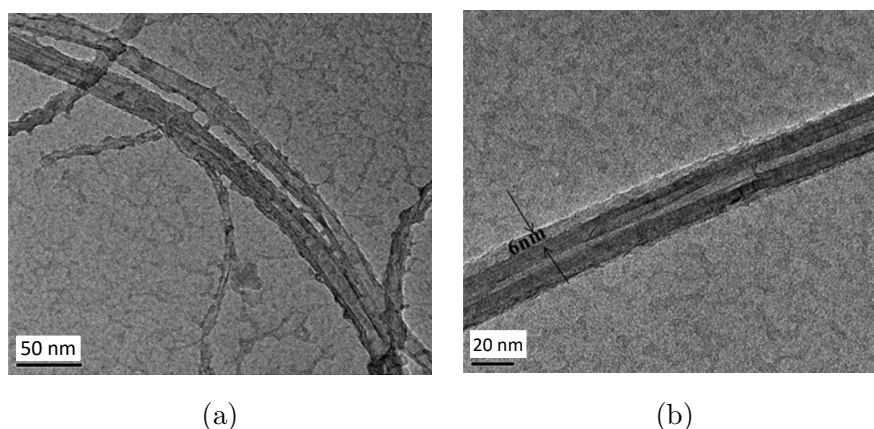


Figure 2.5: HR-TEM (High Resolution Transmission Electron Microscopy), images of MWCNTs dispersed in the mixed surfactant system (SOCT/DTAB), at different scales [22].

Castell et al. [20] published a report in which the main purpose was to obtain a stable dispersion of MWCNTs to incorporate in a polyvinyl alcohol (PVA) composite to improve its thermal properties. To accomplish this, a mixture of two surfactants was used - sodium dodecylbenzenesulfonate surfactant (SDBS), which was efficient to disperse the MWCNTs homogeneously, and polyvinylpyrrolidone polymer (PVP), which adsorbed onto the outer layer of the stabilized MWCNTs-SDBS, hence improving the compatibility of this system with the PVA matrix. When compared to both MWCNTs-SDBS and MWCNTs-PVP systems, the MWCNTs-SDBS-PVP system proved to be better suited for the production of PVA composites, resulting in a final composite with a greater degree of enhancement of its properties.

Sohrabi et al. [23] conducted a study on the ability of cationic-rich and anionic-rich mixtures of surfactants to successfully disperse MWCNTs in aqueous media. The cationic surfactant used was cetyltrimethylammonium bromide (CTAB) and the anionic surfactant was sodium dodecyl sulfate (SDS). In this study it was concluded that a mixture with a ratio of 90:10 CTAB/SDS (cationic rich) was better able to disperse MWCNTs than pure CTAB; in the same way, it was found that a mixture with a ratio 10:90 CTAB/SDS (anionic rich) was better able to disperse MWCNTs than pure SDS. This improvement was attributed to the synergistic effects owed to the electrostatic attractions between surfactant heads of opposite charge.

As referred before, the use of surfactants and polymers is widely popular within this technique, and although there are studies in progress to understand exactly how the surfactant-CNT system behaves [24, 25], it is known that the dispersion involves physical adsorption rather than covalent linkage, therefore maintaining the CNTs chemical bonds

intact. Due to this feature, most of the CNTs intrinsically beneficial properties are not compromised [15].

In spite of this major advantage compared to the covalent functionalization, this method has also some drawbacks. First of all, since the stabilizer molecules cover most of the CNTs surface, the desired reactions may be held back due to physical blocking. An example to take into account, given the purpose of this work, is the blocking of the interaction between CNTs and hydration reaction products in cement composites reinforcement studies [19]. Additionally, some researches have revealed that in some cases a high concentration of surfactant is needed to achieve the required level of dispersion, which in turn may obstruct some of the beneficial effects of adding CNTs to such composite materials [20].

2.1.4 Mechanical dispersion of CNTs

Besides the chemical methods, mechanical methods have also been developed with the purpose of dispersing CNTs. The dispersion of CNTs via mechanical techniques is accomplished mainly through high-shear mixing and ultrasonication. The operation principle behind both of this processes is based on the transfer of local shear stress to break down the aggregates, and the main difference between them is the mechanism for delivering this shear stress [26].

Since high-shear mixing is not a suitable process for dispersing CNTs in aqueous media [26], it will not be discussed in further detail.

On the contrary, ultrasonication plays an important role in aiding the debundling of CNTs in fluids of low viscosity [26]. In this procedure, the first step is the conversion of line voltage to mechanical vibrations (by the ultrasonic processors), which are then transferred into the liquid through the probe, generating pressure waves. Because of this, the formation and implosion of microscopic bubbles occurs, in a process designated as cavitation. Knowing that millions of these bubbles are formed, the energy release upon their collapse is strong enough to be able to disperse objects and/or surfaces within the cavitation field [27].

A few problems are associated with the use of mechanical methods to disperse CNTs. The introduction of an external shear stress in the system will weaken not only the bonds between different nanotubes, but also the carbon bonds within the CNTs, which leads to nanotubes fragmentation and decrease of their aspect ratio (which will impact negatively on their properties) [22, 26]. Moreover, the separation of CNTs from their agglomerates through mechanical techniques are usually time-consuming, and its effects are temporary. Once the energy that is applied to the system is removed, CNTs tend to re-aggregate. However, these techniques, particularly ultrasonication, have proven to be

of great usefulness when used together with a chemical method [22, 26]. For instance, in a non-covalent functionalization, the use of ultrasounds allows the temporary separation of CNTs, enabling the interfacial molecules to come into contact with the CNTs surface, thus promoting its adsorption. This combined use of adsorbent molecules and ultrasounds have been reported by many researchers [27–36].

2.1.5 Nanocomposites

The extraordinary achievements that have been witnessed in the field of nanotechnology have opened the doors to a better understanding of the structure-property relation of most types of materials, and the technological development within this area has allowed their manipulation at the molecular level, hence enabling the tailoring of their properties to meet the requirements of a particular application [8].

Among the most promising materials in this line of research are included the CNTs, due to their impressive properties, already exposed in section 2.1.1. Once solved the CNTs dispersion issue (discussed in the previous sections), one can move forward towards the study of their applicability in the development of many nanocomposites [37].

The incorporation of CNTs in polymer matrices, to improve either their electrical or mechanical properties, was among the first studies conducted on this subject. To date, the research and production of polymer nanocomposites has definitely evolved into one of the biggest areas of application of CNTs, with many commercial applications already available in the market and many more studies being conducted in order to fully explore its potential [2, 15, 37].

Besides polymer composites, the use of CNTs extended to a wider range of fields. One example is the addition of small amounts of CNTs to metals and metallic alloys, to obtain composites with enhanced tensile strength and Young's modulus, and with lower density [2]. Other applications for CNTs nanocomposites include water treatment [38] microelectronic devices, sensors, energy storage, microelectronics and biomedicine applications [16].

Another area in which CNTs became an issue of great interest was the reinforcement of cement based materials. Cementitious materials (of which the most common is Portland cement) are at the core of civil engineering construction, and are known to have a brittle-like behaviour, characterized by low tensile strength, low ductility, and high tendency to suffer cracking [13]. From this arose the need to seek new ways to enhance the properties of these materials, and several studies have been conducted in the past decades to assess the use of numerous types of compounds for this purpose [39, 40].

The successful use of CNTs as reinforcement agent relies on a good interfacial interaction with the composite matrix, for which it is necessary to ensure an appropriate

dispersion. If CNTs are aggregated, there will be a loss of its beneficial properties, due to a decrease in their surface area available to react with the Portland cement matrix [41]. However, in a dispersed state, CNTs have proved to be quite effective to improve the performance of cement composites [17, 39]. These structures are able to act as bridging agents at a nanoscale, hence preventing the further propagation of nanocracks. The use of microfiber reinforcements has been reported to delay the growth of microcracks, however they are not able to completely stop it, as opposed to what happens when nanosized materials are used [17, 39]. In Figure 2.6 the action of CNTs as bridging agents to cease the expansion of nanocracks is evident.

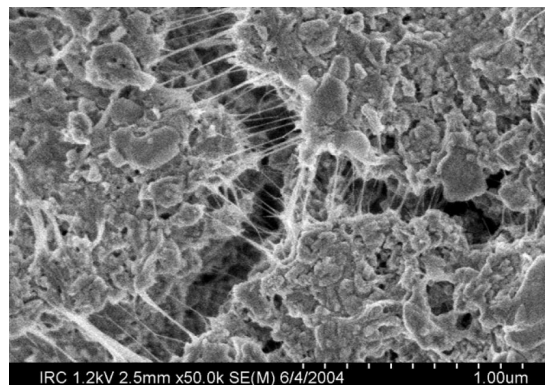


Figure 2.6: Crack bridging by SWCNTs in a hydrated Ordinary Portland Cement/SWCNTs composite [42].

Some authors have been exploring the surface treatment of CNTs as a way to improve their reactivity with the cement matrix, which in some cases has been beneficial to the final composite properties [43, 44], while in other cases this does not happen [18], depending on the experimental conditions used.

Konsta-Gdoutos [27] studied the influence of the length and concentration of MWCNTs incorporated into cement paste on its mechanical properties, as well as the influence of its dispersion conditions. Moreover, the samples were tested at different times of hydration. From this work, it was concluded that an effective dispersion of the MWCNTs required the use of both a surfactant (at a weight ratio of surfactant to MWCNT close to 4) and ultrasonic energy. Once this was attained, the results obtained suggest that in order to achieve the same level of mechanical enhancement of the composite properties, a higher concentration of short MWCNTs (0.08 wt.%) is necessary compared to long MWCNTs (0.048 wt.%), as demonstrated in Figure 2.7. Here the results obtained for flexural strength (Figure 2.7a) and Young's modulus (Figure 2.7b) are shown, in which it is clear that the mechanical behaviour of composites containing 0.08 wt.% short MWCNTs approaches the one from composites containing 0.048 wt.% long MWCNTs.

Several other reports on the use of nanomaterials, in particular CNTs, as reinforcement

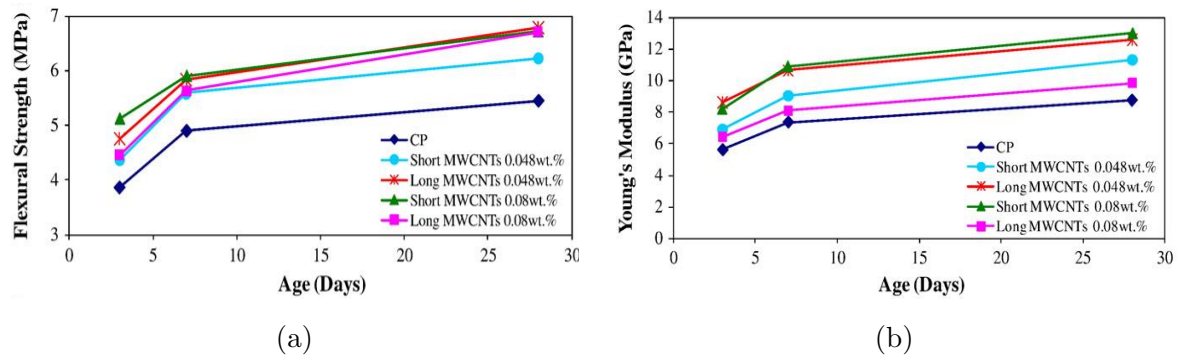


Figure 2.7: Effect of the type and concentration of well-dispersed MWCNTs in the mechanical properties of cement paste composites, with a water/cement ratio equal to 0.5: a) flexural strength; b) Young's modulus [27].

agents to originate high performance cement composites can be found in the literature [17, 19, 35, 36, 43, 45–49].

2.2 Chemical stabilization of soils

Soil stabilization consists on a controlled modification of the soil, through either mechanical or chemical methods, in order to improve its geotechnical properties. The need for such techniques emerged from the pressure to use soils with poor geotechnical characteristics, or simply to tune the soil's properties, making it better suited for its final purpose [50]. For construction works purposes, it is important to ensure that the soil has the appropriate mechanical strength required.

Chemical stabilization methods consists on the addition of cementitious materials, or binders (such as Portland cement, lime and fly ash) to natural soil, hence inducing physico-chemical reactions between the soil particles, the binder and water, which results in a stronger and stiffer composite matrix. This technique depends on several factors (which should be further studied in order to be able to achieve the desired properties) [51] and it is frequently used for the stabilization of soft soils, to improve their behaviour for construction projects [52, 53].

When a binder is mixed with soil, hydration reactions with the water present in the soil immediately begin to occur, followed by pozzolanic reactions (with compounds generated during the hydration process and pozzolanic minerals in the soil) and ionic exchange. These reactions take part in the soil stabilization in two different ways - for one, they generate cementitious products that bind to each other and to the soil particles, and in addition the production of new substances promotes the filling of many of the void spaces in the soil matrix, hence strengthening the final composite material [54].

The most common binder used for soil stabilization is Portland cement. However,

other additives (e.g. blast-furnace slag, fly ash, silica fume) can be mixed with the main binder in order to better suit the soil properties (such as organic matter content, water content and grain size distribution) and the final purpose of the stabilization process [54]. In this context, there has been a growing interest in the use of nanoparticles in this field. Due to their extremely high specific surface area, nanoparticles are able to exert a significant influence in the physical and chemical behaviour of the soil composite properties [55]. CNTs in particular have the potential to enhance the mechanical behaviour of soils, (which is one of the main focus of this work), due to their high flexibility and extraordinary mechanical properties as described in section 2.1.1.

A number of studies regarding the combination of CNTs and Portland cement to yield high performance concrete materials have already been conducted, as referred in section 2.1.5, however, the research on the potential benefits of the incorporation of CNTs in soil-cement composites is very recent, and the only studies found regarding this subject were the ones conducted at the University of Coimbra in the last couple of years [28, 31, 33]. In those studies, the addition of MWCNTs to soil combined with Portland cement resulted in great benefits in the mechanical properties of the final composite material, assessed through unconfined compression strength tests (UCS).

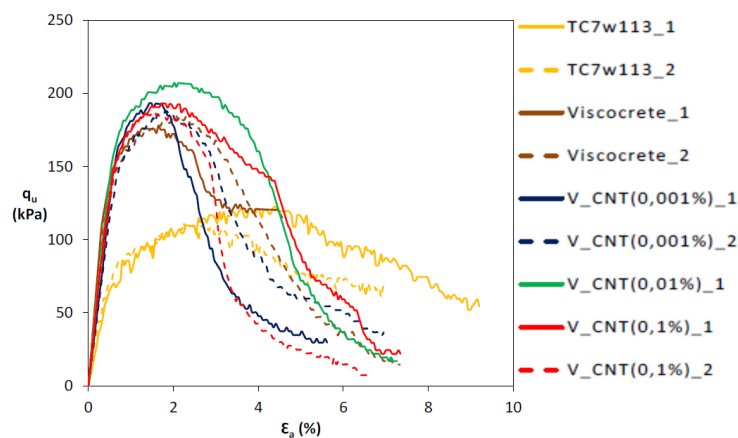


Figure 2.8: Stress-strain plots obtained from UCS tests for samples containing different amounts of MWCNTs dispersed with a solution of Viscocrete 3008 at a concentration of 3% [31].

Casaleiro [31] studied the benefits of incorporating MWCNTs on the mechanical behaviour of the soft soil of *Baixo Mondego*, after their dispersion with a surfactant. Within the tested conditions in this work, it was concluded that the best mechanical performance of the soil was obtained for 0.01% MWCNTs stabilized with 3% Viscocrete 3008, subjected to 5 minutes of ultrasounds. In this case there was an improvement of 77.1% of the unconfined compressive strength with respect to the test stabilized without MWCNTs. Figure 2.8 displays the stress-strain data obtained by the author regarding the study of different amounts of MWCNTs dispersed with a 3% solution of Viscocrete 3008 (an

anionic polymer of medium molecular weight). The curing time for all samples was 7 days.

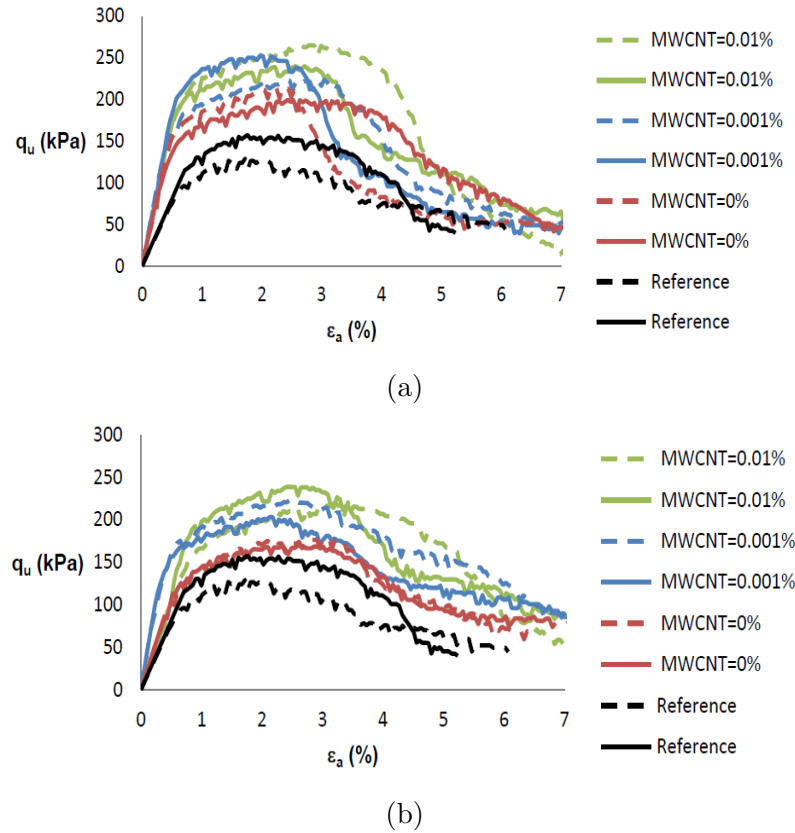


Figure 2.9: Stress-strain plots obtained from UCS tests for samples containing different amounts of MWCNTs, dispersed with a solution of: a) Amber 4001 1%; b) Glycerox 2% [28].

Figueiredo [28] conducted similar studies, testing different surfactants in varied concentrations, and two concentrations of MWCNTs (0.001% and 0.01%). The results obtained from the UCS tests indicated that the mechanical characteristics of the composite material were better enhanced when using either a 1% solution of Amber 4001 with 0.01% MWCNTs or a 2% solution of Glycerox with 0.001% MWCNTs. These surfactants were of cationic and non-ionic nature, respectively; Figueiredo also tested two anionic surfactants, but since they failed to achieve an adequate dispersion of MWCNTs, these were not tested with the soil. In Figure 2.9 the stress-strain plots referring to the UCS test of soil containing 1% Amber 4001 (Figure 2.9a) and 2% Glycerox (Figure 2.9b) enriched with two concentrations of MWCNTs are shown. All samples were cured for 7 days.

Finally, Moura [33] investigated the influence of the type of surfactant and its concentration to disperse two concentrations of MWCNTs (0.001% and 0.01%) and also the influence of different curing times in the mechanical properties of the final soil matrix. The main conclusions drawn from this work were that the addition of MWCNTs to the soil composite showed an adverse effect on the secant undrained Young's modulus (E_{u50});

nonetheless they were capable of improving its unconfined compressive strength. Among the samples tested, the samples comprising 0.1% Amber 2006 (a polyamide) and 0.01% MWCNTs showed an interesting enhancement of mechanical strength in relation to the reference value (soil stabilized without MWCNTs). Figure 2.10 exhibits the stress-strain results for soil composite samples containing 0.1% Amber 2006 with different amounts of MWCNTs, after 7 days of curing.

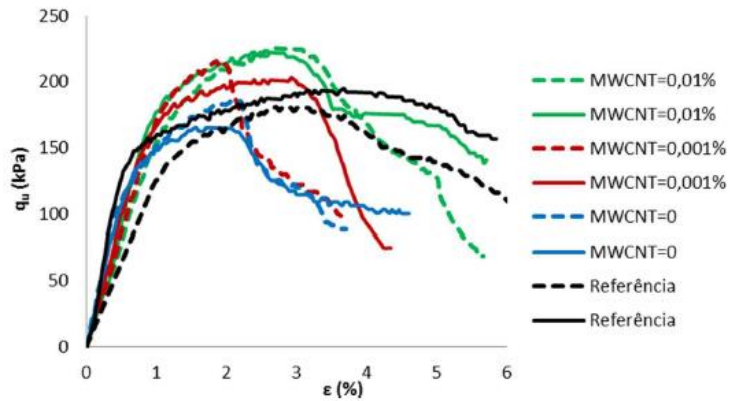


Figure 2.10: Stress-strain plots obtained from UCS tests for samples containing different amounts of MWCNTs dispersed with a solution of Amber 2006 1% [33].

Chapter 3

Materials characterization and experimental methods

The present chapter describes the materials and experimental procedures used in this study. The main goal is to ensure that all the samples tested are prepared in a reproducible and homogeneous manner.

According to the information presented earlier, obtaining a good dispersion of MWCNTs in water can be quite a challenge, and one of the possible solutions to this problem is adding a surfactant to the dispersion and subjecting it to ultrasounds. In this work, several surfactants were tested, where their concentration, ultrasound time and pH were optimised in order to find the best conditions for a good dispersion.

The experimental tests were set off with the characterization of surfactants used, which consisted on the determination of its hydrodynamic diameter, molecular weight and zeta potential. Then, the dispersion conditions were optimised by evaluating the particle size distribution of the MWCNTs dispersions, followed by its addition into the soil chemically stabilized with a binder, after which samples were prepared to perform unconfined compression tests (UCS). These tests allowed to determine whether the mechanical performance of the soil was enhanced due to the addition of MWCNTs-cement composites.

3.1 Materials

3.1.1 Carbon Nanotubes

In this study, multi-wall carbon nanotubes (MWCNTs) produced by Nanocyl were used. According to the manufacturer, the commercial carbon nanotubes CN7000 were produced via Catalytic Chemical Vapor Deposition Process (CCVD), and its properties include an average diameter of 9.5 nm, an average length of 1500 nm and a specific surface area in the range of 250 - 300 m²/g. Their purity, expressed in terms of the amount of carbon present, is around 90%, and the remaining 10% are metal oxides [56]. In a previous work [31], complimentary studies were conducted on the MWCNTs, namely zeta potential and density, showing that they have a negative electrical charge of -25.2 mV and a density of 1.7 g/cm³.

3.1.2 Surfactants

As it was mentioned before, surfactants can be used as an additive to improve carbon nanotubes dispersion in aqueous media. Here, several surfactants were tested, in different concentrations, in order to find the optimal conditions for a good MWCNTs dispersion.

The surfactants Amber 2009, Amber 2012, Amber 2013, Amber 2014 and Glycerox were produced and supplied by aquaTECH, and its specifications are presented in Table 3.1.

Table 3.1: aquaTECH surfactants - data provided by the supplier.

Surfactant	Concentration (wt.%)	Viscosity (mPa s)	Charge
Amber 2009	40	2000 - 3000	Cationic
Amber 2012	>95	35000 (at 40%)	Cationic
Amber 2013	35	>9000	Cationic
Amber 2014	50	>10000	Cationic
Glycerox	31	-	Non-ionic

The Amber polymers are included in the polyDADMACs group (poly dially dimethyl ammonium chloride), which are cationic polyelectrolytes, containing pyrrolidine rings in its structure [57].

This study was complemented with the use of commercial polyDADMACs from Sigma-Aldrich, with high and medium molecular weight - these surfactants will be referred throughout this document as polyDADMAC HMW and polyDADMAC MMW, respectively. In addition, a different type of non-ionic surfactant was tested, and to this end Pluronic F-127 was used, which was also acquired from Sigma-Aldrich. The information about these products, made available by the manufacturer through their Safety Data Sheets, is presented in Table 3.2.

Table 3.2: Sigma-Aldrich surfactants data provided by the supplier.

Surfactant	Concentration (wt.%)	Charge
polyDADMAC HMW	20	Cationic
polyDADMAC MMW	20	Cationic
Pluronic F-127	-	Non-ionic

3.1.3 Binder

As said previously, one of the possibilities to enhance the mechanical performance of a soil is by adding a binder. The choice of which binder to use is undoubtedly dependent on the properties of the soil, and will have an impact on the physico-chemical reactions taking place during the chemical stabilization process [54]. The most common binder used for this purpose is Portland cement, and it was also the binder used for this study, more specifically Portland cement type I, class of mechanical resistance 42.5 (also referred to as CEM I 42.5 R). Table 3.3 shows the composition of this binder. It is also important to point out that cement has a negative charge, exhibiting a zeta potential of -2.14 mV, according to Figueiredo [28].

Table 3.3: Chemical composition of Portland cement (CEM I 42.5R) - data provided by the supplier, CIMPOR.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
Quantity (%)	62.84	19.24	4.93	3.17	2.50	3.35

3.1.4 Soil

The present work was carried out using soil retrieved at a depth of 2.5 m, in an agricultural portion of land located in *Quinta da Foja* reserves, between *Coimbra* and *Figueira da Foz*. After collecting the soil, it was transported to the Geotechnical Laboratory of Department of Civil Engineering of FCTUC, in three boxes of 1 m³ each, protected by plastic sleeves and plastic wrap in order to minimize water loss. The soil was then homogenized in the laboratory, according to the procedure described in [31]. In order to guarantee that representative samples were prepared, the amount of soil necessary to the completion of this work was subjected to another process of homogenization, with a Sammic BM-11 mixer, and stored in a thermo-hygrometric chamber at controlled temperature of $20 \pm 2^\circ\text{C}$ and relative humidity of $90 \pm 5\%$.

This soil is classified as a soft soil, due to its low undrained shear strength, high plasticity and high compressibility, which means that its geotechnical characteristics are very weak. In addition, it contains a high amount of organic matter (7.41%, determined according to the BS 1377-3 (1990) standard [58]) which can be a disadvantage for the chemical stabilization process, due to the retention of calcium ions, which can affect the hydration reactions of the binder.

The water content of the soil is another variable of major importance to this study, since it has a great impact on the hydration reactions taking place. Correia [54] determined

that the natural water content of this particular soil was 80.87%. After the homogenization process, the water content of the soil was measured [59], and the required amount of water was added to keep this value constant at around 80.87%. Bearing in mind that this study deals with molecular compounds that are sensitive to pH, namely polyDADMAC surfactants, the pH of the soil was also measured, obtaining a value of 5.34.

Additionally, other tests were conducted on the soil in order to have a full material characterization before proceeding with the intended study. The methodology used is not described in detail, since it is included in the standards referred below. A full description on the tests used for the soil characterization can be found in the works of Correia [54] and Casaleiro [31].

Besides the water content and organic matter content already mentioned, the density of the soil particles was determined, according to the NP-83 (1965) standard [60], obtaining a value of 2.61. This corresponds to the ratio between the mass of a given volume of particles at the temperature in which the test is conducted and the mass of equal volume of distilled water at 20°C.

The Atterberg limits were also determined in accordance with the NP-143 (1969) standard [61], with dried soil. These limits establish the boundaries between different behaviours of the soil according to its water content. The liquid limit obtained was 54.1% and the plastic limit was 39.8%.

Finally, a study on the granulometric composition of soil was carried out. The E 196-1966 standard [62] was used for this purpose, and the grain size distribution obtained showed that this soil contains 21% clay, 59% silt and 20% sand. The granulometric curve can be seen in Appendix A.

3.2 Experimental methods

3.2.1 Characterization techniques

In order to better understand the possible interactions occurring during the studies conducted in this work, a series of tests were performed to determine several properties of the materials used, which could turn out to be of great importance to shed some light on the final results obtained.

The equipment used to run the majority of tests was the Zetasizer Nano Series (ZNS), manufactured by Malvern Instruments Ltd, through which it is possible to measure the hydrodynamic diameter, molecular weight and zeta potential of particles or large molecules. In addition, the refractive index of the solutions was also measured.

Hydrodynamic diameter

The hydrodynamic diameter is a parameter that can be used to describe the size of particles present in a sample. When considering a suspension of particles, their shapes will most likely not be spherical, however, in terms of data analysis, it is much simpler to have the size described by only one value, which is only possible if the shape considered is a sphere. Therefore, the hydrodynamic diameter is defined as the diameter of an equivalent spheric particle that diffuses in the liquid media at the same speed of the particle being measured. The ZNS equipment makes use of the Dynamic Light Scattering (DLS) technique to achieve this quantity, which in return is based on two principles - Brownian motion and scattering intensity fluctuation.

Particles suspended in a liquid are not static, in fact they are constantly bombarded by the solvent molecules surrounding them causing a random movement, designated Brownian motion. The speed of this movement is dependent on the particle size - the larger the particle, the slower it moves.

When a light source (such as a laser) crosses their path, the light is scattered and the speckle pattern created is detected. As the particles are continuously moving, this pattern will change over time, which means that there will be an intensity fluctuation of the light scattered, and the rate at which this occurs is related to the size of the particles. The smaller particles move more quickly, so the intensity fluctuation rate is higher, and the opposite happens with larger particles. The fluctuation in scattering intensity detected is then converted into particle size through a digital correlator within the equipment. This component determines the degree of similarity between two signals over a period of time, and the more similar the signals are, the stronger is the correlation between them. Due to the Brownian motion, that keeps the particles moving randomly in the suspension, the correlation of a signal tends to decrease over time, and the rate of this decay is related to the particle size - if the particles are smaller, they will move faster, the intensity fluctuation rate will be higher and the correlation between signals over time will decrease more rapidly. Figure 3.1 displays typical correlation functions for large and small particles.

In order to obtain the size values from the correlation function, two algorithms can be used: the cumulants analysis, which fits the correlation curve to an exponential function or the CONTIN method which fits the correlation curve to multiple exponential functions; the latter is usually employed for more complex samples. Through one of these algorithms, the translational diffusion coefficient, D_e , is calculated, and this variable is then related to the hydrodynamic diameter by Stokes-Einstein equation (equation 3.1).

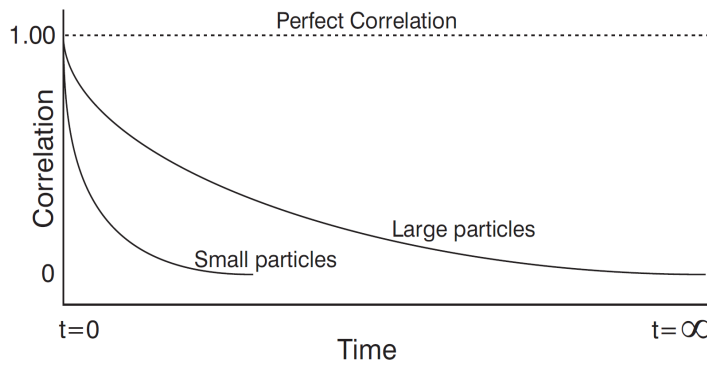


Figure 3.1: Correlation functions for large and small particles [63].

$$D_c = \frac{kT}{3\pi\mu D_h} \quad (3.1)$$

where k is the Boltzmann constant, T is the absolute temperature, μ is the dynamic viscosity and D_h is the hydrodynamic diameter.

From the above theory, a size distribution is obtained, which is used to evaluate the average diameter of the distribution, D_z or Z-average, i.e., the averaged particle size. The ZNS software assumes that the dispersion of particles obey the Rayleigh theory, which states that the intensity of the scattered light is proportional to D_i^6 , and the value of D_z is then given by equation 3.2.

$$D_z = \frac{\sum I_i}{\sum \frac{I_i}{D_i}} \quad (3.2)$$

where D_z is the intensity weighted harmonic mean size of the hydrodynamic diameter distribution, I_i is the scattered light intensity of class i and D_i is the hydrodynamic diameter of class i .

When preparing a sample to determine the D_z , it is necessary to take some aspects into consideration, among which the most important one is the concentration of the solution prepared. It must be assured that the concentration is high enough to enable the equipment to perform the measurement, but not so high as to cause multiple scattering effects and aggregation of particles. The parameter *count rate*, available in the ZNS software, gives an indication of whether the concentration used is appropriate, as well as the *quality report*, in which potential problems with the measurement are stated [63, 64].

Molecular weight

Since polymer compounds are comprised of several repetition units (monomers), the determination of its molecular weight, which is directly related to the chain length (and

therefore size), becomes of great importance in their characterization and also in understanding how the molecules may behave in the experimental environment in question.

The molecular weight measurement of macromolecules in the ZNS equipment is possible to achieve using the Static Light Scattering (SLS) technique. Similarly to DLS, in SLS the laser illuminates the particles in a sample, which will scatter the incident light in all directions. The main difference between these two methods is that DLS measures the time fluctuations in the scattering intensity, whereas SLS uses the time-averaged intensity of the scattered light. Performing this measurement is only possible as long as the particle size is small enough so that the light is scattered isotropically, and the angular dependence of the measured intensity is minimized, allowing the measurement of molecular weight by a single angle static light scattering technique. In this case, the intensity of light scattered by a particle in solution can be described by the Rayleigh equation 3.3, presented below.

$$\frac{KC}{R_\theta} = \left(\frac{1}{MW} + 2A_2C \right) P_\theta \quad (3.3)$$

where R_θ is the Rayleigh ratio (ratio of scattered light to incident light on the sample), C is the concentration, MW is the molecular weight, A_2 is the 2nd virial coefficient, P_θ is the angular dependence of the sample scattering intensity and K is an optical constant defined by the following equation:

$$K = \frac{2\pi^2}{\lambda_o^4 N_A} \left(n_o \frac{dn}{dc} \right)^2 \quad (3.4)$$

where N_A is the Avogadro's constant, λ_o is the laser wavelength, n_o is the solvent refractive index, and dn/dc is the differential refractive index increment (change in refractive index as a function of the change in concentration).

The Rayleigh ratio (R_θ) refers to the ratio between the scattered and incident light intensity on the sample. Due to the inherent difficulty of measuring the magnitude of the incident light interacting with the particles, the standard approach consists of relating the measurement of the scattering intensity of the analyte to that of a reference with a well-known Rayleigh ratio. To this purpose, toluene is commonly used, since it has proven to be suitable for precise measurements, and its Rayleigh ratios are well-known over a broad range of wavelengths and temperatures. The expression used to calculate the sample Rayleigh ratio from a toluene standard is given by equation 3.5.

$$R_\theta = \frac{I_A n_o^2}{I_T n_T^2} R_T \quad (3.5)$$

where I_A is the residual scattering intensity of the analyte, I_T is the toluene scattering intensity, n_T is the toluene refractive index, and R_T is the Rayleigh ratio of toluene.

The 2nd virial coefficient (A_2) is a variable used to describe the interaction strength between the particles and the solvent - in other words, it can quantify the solubility of the molecules.

As mentioned before, the P_θ term relates to the angular dependence of the sample scattering intensity. When the particles are large enough to accommodate multiple photon scattering, there are both constructive and destructive interferences of the light scattered from different positions on the same particle (Mie scattering). In contrast, if the particles in solution are much smaller than the wavelength of the incident light, the multiple scattering phenomenon is minimized and P_θ will reduce to 1 (meaning that there is no longer an angular dependence of the scattering intensity) and Rayleigh scattering can be assumed.

According to the Rayleigh theory, the intensity of scattered light produced by a particle is proportional to the product of the weight-average molecular weight and the concentration of such particles. Thus, the Rayleigh equation must be applied over a range of different concentrations of the sample in order to obtain the Debye plot, which is a representation of the intensity of the scattered light (K/CR_θ) versus the concentration of the sample used to do each measurement. This plot contains two lines, namely the Debye line and the intensity line. The former allows to determine both the molecular weight, from its interception with the Y axis (K/CR_θ), that provides the value of $1/MW$, and the 2nd virial coefficient from its slope; while the latter can give information on whether multiple scattering effects are present (this will be true if the intensity of the scattered light decreases between two consecutive points of increasing concentration). An example of a typical Debye plot is shown in Figure 3.2.

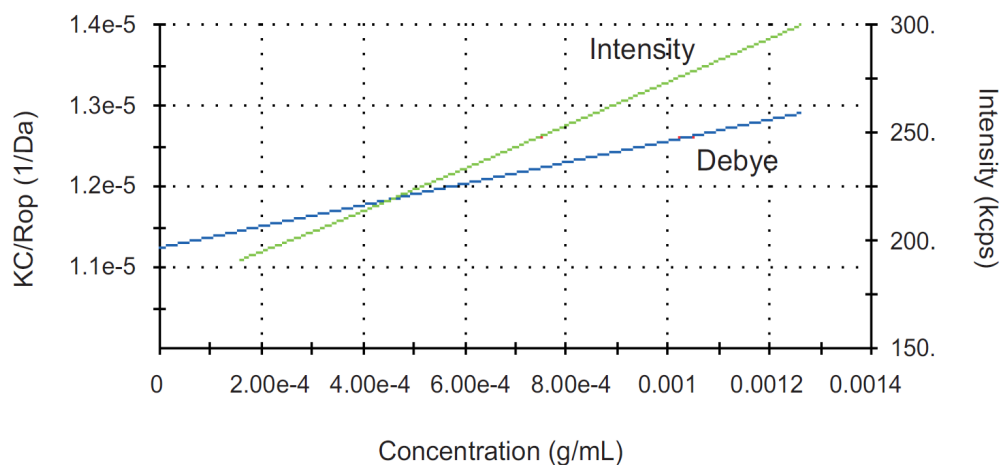


Figure 3.2: Debye Plot [63].

Before starting the molecular weight measurement of a sample, it is necessary to determine its differential refractive index increment as well as its hydrodynamic diameter,

which will then be introduced in the ZNS software to perform the measurement [63, 65].

Refractive index

The refractive index (RI) is defined as the ratio between the speed of light in vacuum and the speed of light in a certain medium. In the previous subsection, it was stated that the molecular weight measurement of a sample must be preceded by the determination of the differential refractive index increment (dn/dc). To this end, the Atago RX-5000 CX Refractometer was used to measure the refractive index of different concentrations used to measure the molecular weight of a sample.

The measurement of the RI was made at a temperature of 25°C, and it started with the calibration of the equipment, placing two drops of the solvent used - in this case NaCl with a concentration of 0.1 M - in the cell for measurement of its RI. After this, two drops of each solution, with different concentrations, were placed in the measuring cell one by one, and between each measurement the cell was carefully cleaned with optical paper to avoid scratching. The values of RI obtained were then plotted against the sample concentrations, and a linear regression was made in order to obtain the value of dn/dc , which corresponds to its slope.

Zeta Potencial

The zeta potential is a parameter used to evaluate the stability of colloidal systems, such as the dispersion of solid particles in a liquid medium, as studied in this work.

When a charged particle is suspended in a liquid, ions of opposite charge (counter ions) tend to travel to its surroundings, creating an electrical double layer around the particle, which is divided into an inner region, the Stern layer (where ions are strongly bound to the particle) and an outer region, the diffuse layer (where ions are weakly bound to the particle). Within the diffuse layer, there is a boundary which divides the ions that are still strongly connected to the particle, in such a way that they follow its movement, and the ions that are not so strongly attracted to it - this is known as the shearing plane. The zeta potential corresponds to the potential at this boundary.

A suspension in which all particles have a large value of zeta potential (that can be either positive or negative) tends to be more stable than a suspension with lower values of zeta potential, given that in the first case the heavily charged particles tend to repel each other rather than aggregate. Generally, if the zeta potential of a sample is either higher than +30 mV or lower than -30 mV, the suspension is considered to be stable.

For this study, the zeta potential was measured in the ZNS equipment, making use of the Electrophoretic Light Scattering (ELS) method. Here, an electric field was applied to the sample, causing the charged particles to be attracted and migrate towards the

electrode of opposite charge. The velocity of this movement, known as electrophoretic mobility, is measured using Laser Doppler Velocimetry (LDV), and it depends on the strength of the electric field applied, the dielectric constant and viscosity of the medium, and the zeta potential of the particles. Afterwards, the Henry equation (3.6) is applied to determine the zeta potential:

$$U_E = \frac{2\varepsilon z f(ka)}{3\mu} \omega r \quad (3.6)$$

where z is the zeta potential, U_E is the electrophoretic mobility, ε is the dielectric constant, μ is the dynamic viscosity and $f(ka)$ is the Henry's function. When this measurement is made in aqueous media, $f(ka)$ takes the value 1.5 (Smoluchowski approximation).

One of the most significant properties of the solution that affects the zeta potential is its pH, therefore all samples for zeta potential measurements were prepared using ultrapure water as the solvent [63].

3.2.2 Characterization of surfactants

The characterization of surfactants used to disperse MWCNT consisted on the determination of its hydrodynamic diameter, molecular weight and zeta potential. To guarantee that the results presented are reproducible and trustworthy, all measurements were performed at least twice, and the final result considered is the arithmetic average of all results obtained for the same conditions.

For the hydrodynamic diameter measurements, a 50 mL solution of surfactant was prepared. Several concentrations were tested, until the optimum for each surfactant was found; it is important to outline that all concentrations referred in this work are specified by weight (for instance, a 0.1 % solution corresponds to 0.1 g/100 mL). Initially, the solvent used for this purpose was ultrapure water, however the results obtained were not within the quality parameters required. Knowing that we are dealing with charged molecules, there are long-range Coulomb interactions acting on the particles, which may affect the results obtained from DLS and SLS techniques. In order to solve this problem, a salt solution was used as solvent, more specifically NaCl with a concentration of 0.1 M, which allowed to screen the disturbing charge interactions in the polyelectrolyte, avoiding the coiling of the polymer molecules [66]. This solvent was used to prepare all solutions to determine both hydrodynamic diameter and molecular weight of the polyDADMAC surfactants; for Pluronic F-127 the solvent used was ultrapure water, since this is a non-ionic compound, and therefore good results were obtained without the need of a different solvent.

The solutions prepared were then stirred for over 12 hours, at 500 rpm, to ensure a

homogeneous dispersion of the surfactant throughout the solution. To assess the particle size, a squared glass cell was filled with the surfactant solution with the help of a syringe with a $0.45 \mu\text{m}$ filter attached to its tip, to prevent the presence of foreign particles in the sample; this cell was then inserted into the ZNS equipment for testing.

Prior to the filling process, some of the samples were also subjected to 2 minutes of ultrasounds, and in the case of Amber 2014 the solution was also heated for approximately 1 hour, then left to cool down while stirring, before being subjected to ultrasounds to eliminate any aggregates. Table 3.4 shows the optimal conditions found for the hydrodynamic diameter measurements of the polymers tested.

Table 3.4: Optimal conditions for the hydrodynamic diameter measurements of all surfactants tested.

Surfactant	Concentration	Solvent	US*	Heating	Stirring
Amber 2009	0.1 %	NaCl 0.1 M	2 minutes	-	$\simeq 12$ hours 500 rpm
Amber 2012	0.1 %	NaCl 0.1 M	2 minutes	-	$\simeq 12$ hours 500 rpm
Amber 2013	0.025 %	NaCl 0.1 M	2 minutes	-	$\simeq 12$ hours 500 rpm
Amber 2014	0.05 %	NaCl 0.1 M	2 minutes	35°C	$\simeq 12$ hours 500 rpm
polyDADMAC HMW	0.1 %	NaCl 0.1 M	-	-	$\simeq 12$ hours 500 rpm
polyDADMAC MMW	0.1 %	NaCl 0.1 M	-	-	$\simeq 12$ hours 500 rpm
Pluronic F-127	0.5 %	Ultrapure water	-	-	$\simeq 3$ hours 500 rpm

*ultrasound time

Figure 3.3 depicts an example of the intensity distribution plot resulting from the ZNS analysis for Amber 2009 size determination. All distribution plots for the remaining polymers are shown in Appendix B.

To determine the molecular weight, several solutions of different concentrations were prepared for each surfactant. The refractive index (RI) was then determined for all of them, in order to build a plot of RI versus concentration, which allowed to determine the value of dn/dc , i.e., the slope of the regression line as described in section 3.2.1 on refractive index, necessary to insert in the ZNS software before the MW measurements. The plots for all surfactants studied are presented in Appendix C. Besides the dn/dc

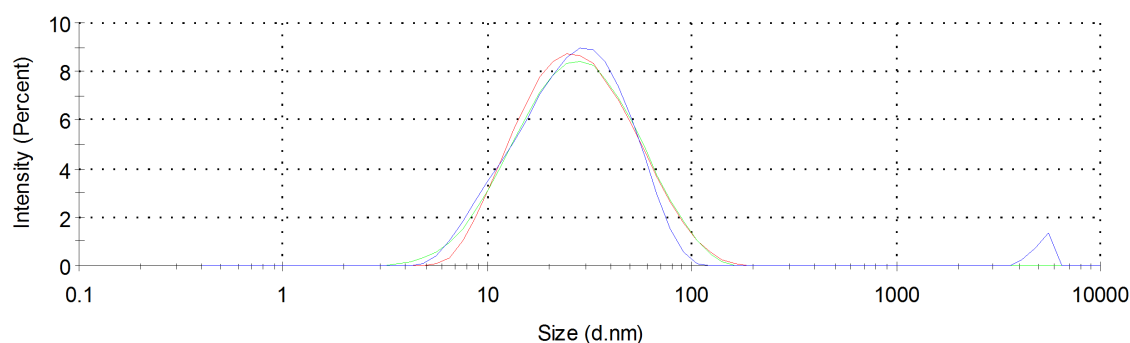


Figure 3.3: Size distribution by intensity for Amber 2009.

value, it is also necessary to insert the value of each concentration used to perform the measurements, so that the ZNS software can generate the Debye plots for the molecular weight calculus. Each sample of different concentration was filtered with a $0.45 \mu\text{m}$ filter when placed in the glass cell, similarly to the procedure followed for the size measurements. All Debye plots are presented in Appendix D.

The evaluation of zeta potential was conducted with solutions in the following concentrations: 0.1% Amber 2009, 0.2% Amber 2013, 0.2% Amber 2014, 1% Amber 2012, 0.2% polyDADMAC HMW, 1% polyDADMAC MMW, and 0.5% Pluronic F-127. Again, these samples went through a $0.45 \mu\text{m}$ filter before filling the electrode cell used for testing. Knowing that in this case the variable of interest is directly related to the particle charge, the solvent used was ultrapure water, instead of the NaCl solution that was used for hydrodynamic diameter and molecular weight measurements, thus avoiding an extra source of charges present in the sample which would greatly compromise the final results obtained. All zeta potential distribution graphics can be found in Appendix E.

Table 3.5 exhibits a summary of the results obtained for the all characterization tests made on the polymers studied. Averaged values are indicated with the superscript ^{av}. All measurements conducted in the ZNS equipment were carried out at a temperature of 25°C in the chamber, and it was always assured that the cells used were clean and without any air bubbles, since the equipment is highly sensitive.

The molecular weight result obtained for polyDADMAC MMW is in good agreement with the data provided by the manufacturer (which states that this value should be between 200-350 kDa), while the result obtained for polyDADMAC HMW is much lower than the range of values defined by the manufacturer (400-500 kDa).

The values of hydrodynamic diameter and zeta potential for Pluronic F-127 were provided by Ana Rita de Oliveira (2016). It is worth pointing out that in the case of Pluronic F-127 the values obtained for molecular weight did not meet the quality criteria, according to the ZNS software. This may be due to the fact that Pluronic F-127

Table 3.5: Characterization of the polymers tested.

Surfactant	D_z (nm)	D_z^{av} (nm)	MW (kDa)	MW^{av} (kDa)	Z (mv)	Z^{av} (mv)
Amber 2009	23.03		35.40		48.20	
	22.93	23.31	38.80	37.47	48.60	48.00
	23.96		38.20		47.10	
Amber 2012	50.42		235.00		74.10	
	51.55	51.19	248.00	238.67	72.20	73.20
	51.59		233.00		73.30	
Amber 2013	46.13		156.00		20.80	
	45.11	45.30	162.00	160.00	20.60	20.10
	44.67		162.00		18.90	
Amber 2014	38.43		59.80		73.70	
	37.85	37.86	55.60	53.07	73.00	72.30
	37.29		43.80		70.10	
polyDADMAC HMW	34.94		143.00		37.40	
	35.35	35.12	146.00	145.33	38.80	39.10
	35.07		147.00		41.00	
polyDADMAC MMW	48.87		201.00		70.10	
	48.13	48.58	269.00	240.00	69.00	69.50
	48.74		250.00		69.30	
Pluronic F-127	6.91		8.18		-0.46	
	6.950	6.92	10.00	9.49	-0.35	-0.43
	6.911		10.30		-0.47	
Glycerox	41.870		4950.00		-	
	41.980	41.93	3580.00	4265.00	-	-

revealed to be a very small molecule (as evidenced by its hydrodynamic diameter), and so the evaluation of its molecular weight might be outside of the detection limit of this equipment.

The characterization of Glycerox can be found in Figueiredo's work [28].

3.2.3 Characterization of MWCNTs dispersions

The parameter used to evaluate MWCNTs dispersions was size distribution, given that we are interested to know if the surfactant was efficient in keeping the nanotubes apart from each other, avoiding the presence of aggregates; this is proved to be true if the average diameter of the distribution (D_z or Z-average) measured is close to the size of a

single nanotube. Obviously, there will always be a certain degree of aggregation; however the presence of the surfactant should minimize these effects.

In order to assess the MWCNTs size distribution, 150 mL solution of surfactant was prepared. The solution was enriched with 0.001% MWCNT and subjected to ultrasonic energy to promote the MWCNTs dispersion. In previous studies [31], the optimum ultrasonication time was determined to be 5 minutes, however, in this study, this ultrasound time proved to be inefficient to successfully disperse the MWCNTs, and so it was adopted an ultrasonication time of 10 minutes for all samples.

A probe-sonicator (Sonics Vibracell 501) with a frequency of 20 kHz and 500 W power was used to perform MWCNTs dispersion. The apparatus for this procedure (Figure 3.4c) included an external circuit of coolant water, to which crushed ice was continuously added in order to control the temperature of the MWCNTs suspension, thus preventing an increase that could have a negative impact in the MWCNTs dispersion, as described in Casaleiro's work [31].

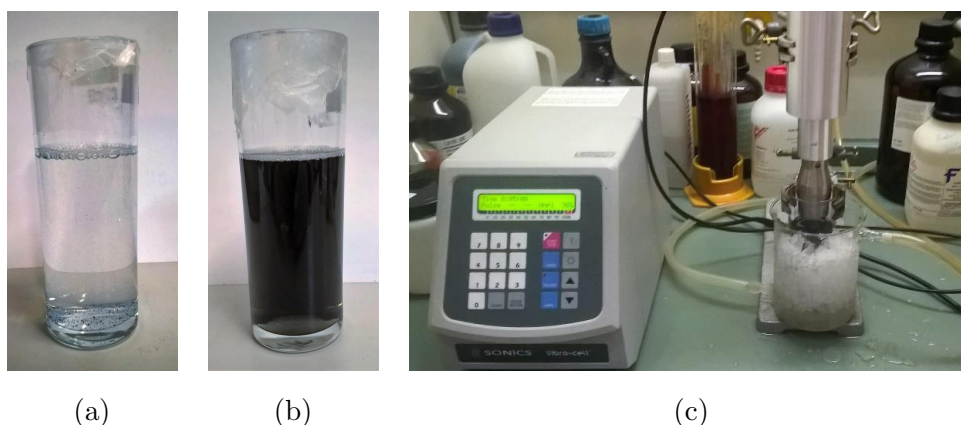


Figure 3.4: a) MWCNTs dispersion before applying ultrasounds; b) MWCNTs dispersion after applying ultrasounds; c) Apparatus used to apply ultrasounds.

Besides the ultrasonication time, a study on the influence of the surfactant solution's pH on the MWCNT dispersion was performed, from which it was concluded that the dispersion of MWCNT with the polyDADMAC polymers was significantly improved for pH values around 7. This is corroborated by a study conducted by Gao et al. [67], in which CNTs in aqueous solutions were successfully destabilized, as part of an experimental removal process, provided that the pH was either in a strongly acid or alkaline range; for the neutral zone the CNTs were maintained dispersed. In the case of Pluronic F-127, the dispersion was effective without the need to adjust the pH.

Finally, the size determination in the ZNS equipment was based on the DLS technique; after the pH correction and ultrasonication, a squared glass cell was filled with the MWCNT dispersion with a pasteur pipette, and the hydrodynamic diameter was mea-

sured, as described in 3.2.1. These results will be analysed and discussed in the following chapter.

3.2.4 UCS test

The main purpose of this work is to investigate how the mechanical performance of the soil chemically stabilized changes after the addition of small amounts of MWCNTs. To this end, unconfined compression strength tests (UCS) were carried out, prepared based on two distinct procedures - sample preparation and sample testing.

Sample preparation

To start the sample preparation, the soil was removed from the thermo-hygrometric chamber and manually homogenized, thus guaranteeing that the sample was representative of the entire soil.

Approximately 900 g of soil was weighted, and 60 g were immediately placed in two capsules used for water content analysis, leaving 840 g of soil in the mixing bowl, to which it was added the binder (Portland cement) already mixed in a beaker with the suspension under study (water only for the reference test; water with surfactant or water with surfactant and MWCNTs). The amount of binder used was 98.94 g (in order to achieve a concentration of 175 kg of binder per cubic meter of soil) and the volume of the suspension was 150 mL.

The mixture was performed in a mechanical mixer (Hobart N50), at a rate of 136 rpm, during 3 minutes. After the first 90 seconds, the mixing process was stopped to move down the material that adhered to the walls of the bowl, and then the process carried on for the remaining time. With this stage completed, two small portions of the mixture were withdrawn without delay, in order to assess the water content immediately after mixing.

Six layers of around 35 g each were weighted and introduced one by one into a PVC mould, with an inner diameter of 37 mm and height of 110 mm. In order to promote a better compaction of the soil and eliminate air bubbles, a slight compression was applied with a circular plate after the introduction of each layer, along with the application of 5 taps.

Afterwards, the soil sample was transferred to the final PVC pipe mould, with an inner diameter of 37 mm and height of 325 mm. Its inner walls were previously covered with a thin grease of vaseline, so as to aid the demolding process later on. The base of the pipe was sealed with duct tape, with a geotextile filter glued to it. Four small holes were made in the duct tape to allow the drainage. Another geotextile filter was also put on the top of the sample inside the mould.

The PVC moulds containing the samples were then placed in a vertical position on a curing tank filled with water, at a temperature of $20 \pm 2^\circ\text{C}$. During this time, a vertical pressure of 24 kPa was applied at the top of the samples with the purpose of simulating the vertical effective stress in the field at a depth of 5 m. Figure 3.5 depicts the several stages of the procedure described above.

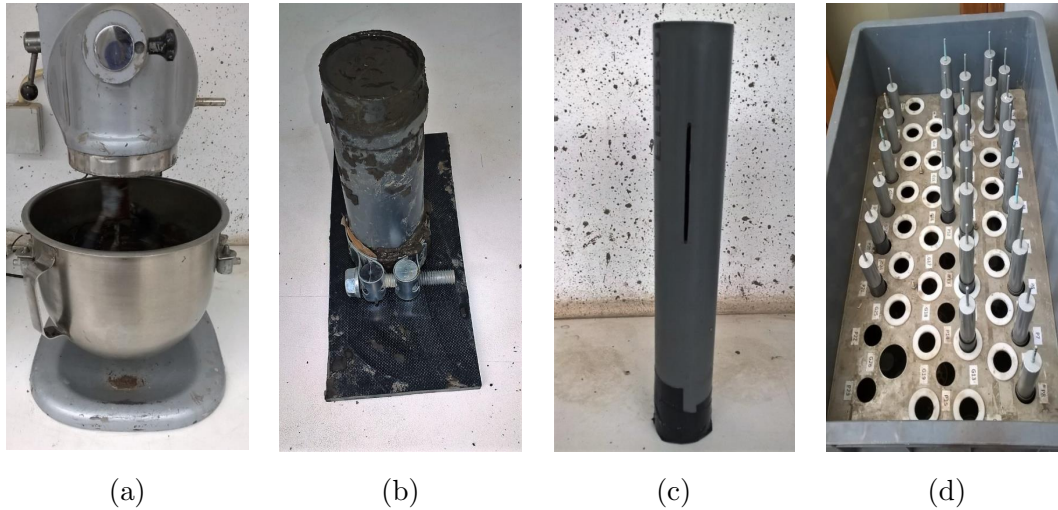


Figure 3.5: Different stages of UCS sample preparation: a) mixing ; b) introduction in the PVC mould; c) final sample; d) curing tank.

Sample testing

After 7 days in the curing tank, the samples were demolded using an hydraulic extractor, and then their height was corrected, in order to have a final sample with 76 mm in height (H) and 37 mm in diameter (D). The sample was weighted, in order to determine its density, and then it was placed on the testing apparatus, making sure that it was centred, so that the force was applied uniformly. During the test, a constant deformation rate was applied, which was previously set to 0.76 mm/min, corresponding to a deformation rate of 1%/min in relation to the height of the sample.

The equipment used to perform this test (Wykeaham Farrance, model Tristar 5000kg) automatically recorded the force (F) applied to the sample as a function of its vertical displacement (δ_v), using a load cell and a displacement transducer. The test is carried out until the failure occurs. Afterwards, two pieces of the broken specimen are gathered for final water content measurement.

The value of force obtained was converted into stress or unconfined compressive strength (q_u) by using equation 3.7.

$$q_u = \frac{F}{A_c} \quad (3.7)$$

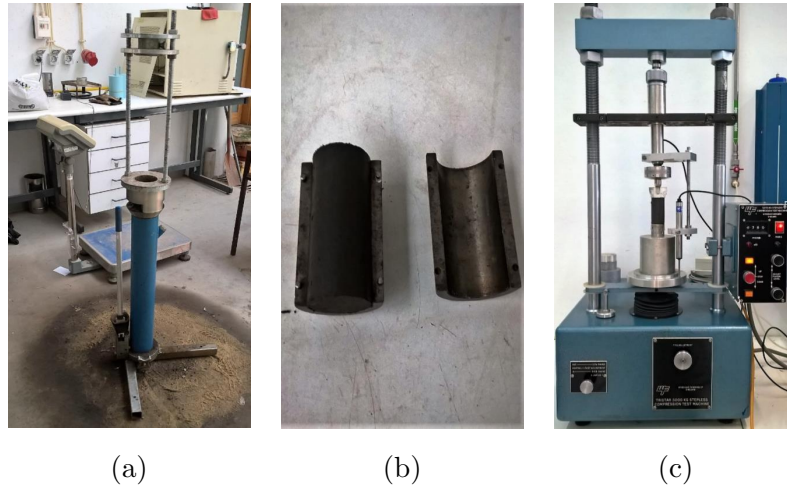


Figure 3.6: Different stages of the UCS test: a) extraction ; b) correction of the sample height; c) ucs test apparatus.

where A_c is the corrected cross-sectional area of the sample, which takes into account the radial deformation of the sample during the test, and it is expressed by equation:

$$A_c = \frac{\pi D^2}{4 \left(1 - \frac{\varepsilon}{100}\right)} \quad (3.8)$$

where ε is the vertical strain, defined by equation 3.9, assuming the hypothesis of uniform distribution of deformation in the sample is valid. In this equation, $\Delta\delta_v$ is the variation of the axial deformation and h is the height of the sample.

$$\varepsilon = 100 \left(\frac{\Delta\delta_v}{h} \right) \quad (3.9)$$

The most important parameter given by this experiment is the maximum unconfined compressive strength ($q_{u_{max}}$). Additionally, from the values of the force and vertical deformation it is built the stress-strain plot ($q_u-\varepsilon$). This allows for a better visualization of the sample's behaviour under unconfined compression.

3.3 Test plan

In order to assess the effectiveness of the chemical stabilization of soil with the addition of the MWCNTs dispersions under study, a series of UCS tests were conducted, allowing to evaluate the mechanical behaviour of the final composites. The UCS tests plan is described in Table 3.6.

This plan was built taking into account the concentrations of surfactants which proved to be capable of better dispersing the MWCNTs (these results are explained in more detailed in chapter 4). Initially, a reference test was made, using only soil, water and

Table 3.6: Tests plan.

Surfactant	Concentration	MWCNT
-	-	-
Amber 2009	0.1 %	- 0.001 %
Amber 2012	0.1 %	- 0.001 %
Amber 2013	0.1 %	- 0.001 %
Amber 2014	0.1 %	- 0.001 %
polyDADMAC HMW	0.1 %	- 0.001 %
polyDADMAC MMW	0.1 %	- 0.001 %
Pluronic F-127	0.1 %	- 0.001 %
Pluronic F-127 + polyDADMAC MMW	0.1 % *	- 0.001 %
Glycerox + polyDADMAC MMW	0.1 % *	- 0.001 %

*This value corresponds to the total concentration of surfactant in the mixture.

The surfactants are used with a ratio 1:1.

binder. Each of the samples prepared with the addition of either a surfactant solution or a surfactant-MWCNTs dispersion were then compared to the reference, in order to evaluate if there was an improvement in their mechanical strength. The amount of binder was kept constant for all tests (175 kg/m³ of soil).

Each test involved the preparation of two samples, at the same time, and in the exact same conditions. The results of the test were only considered valid if the range of variation of q_{umax} was below 15% of the average of the two values of q_{umax} obtained.

Chapter 4

Results and Discussion

In this chapter, the results regarding the efficiency of MWCNTs dispersions in aqueous media, as well as their incorporation into the soft soil to improve its mechanical properties are presented and discussed. The experimental procedures, described in detail in the previous chapter, were rigorously followed in order to minimize the experimental errors and ensure reproducible results.

All concentrations are specified by weight, as mentioned in the previous chapter.

4.1 MWCNTs dispersions

As mentioned in chapter 2, in order to guarantee that the beneficial properties of MWCNTs are not lost due to their agglomeration, an appropriate dispersion of these particles must be ensured before investigating their applicability in nanocomposite materials.

For that, seven different surfactants (Amber 2009, Amber 2012, Amber 2013, Amber 2014, polyDADMAC HMW, polyDADMAC MMW and Pluronic F-127) and two surfactant mixtures (Pluronic F-127 with polyDADMAC MMW and Glycerox with polyDADMAC MMW) were tested in an attempt to achieve a good dispersion of MWCNTs. The quality of these dispersions was assessed through the DLS technique (described in section 3.2.1), by measuring the hydrodynamic diameter (D_z) of the particles in suspension - if this value is too high, or if the size distribution curve exhibits more than one peak, or even if the size distribution peak is too wide, it can be concluded that aggregates are present.

The concentration of MWCNTs used for this work was 0.001%. This value was defined by the ratio of MWCNTs to the dry weight of cement, meaning that this concentration corresponds to 0.001 g of MWCNT/ 98.94 g of Portland cement.

At the beginning of the experimental work, the ZNS equipment was not available to perform a size distribution analysis of the particles in suspension, and so a pre-screening of the optimal conditions to obtain a good dispersion was conducted based on a qualitative analysis. In this context, the Amber surfactants were the first ones to be tested, at three different concentrations (1%, 0.5% and 0.1%), applying 5 minutes of ultrasonic energy (based on Casaleiro's work [31]) and without any change in the pH. However, these conditions proved to be inefficient to disperse the MWCNTs for some of the samples prepared, and thus it was decided to perform additional tests, with the same concentrations mentioned above, but this time subjecting the samples to 10 minutes of ultrasonic energy and

assessing the effect of the pH. For this purpose, the samples were tested with their natural pH (which varied between 4 and 6, depending on the surfactant and its concentration in the solution) and also with a pH modification of the surfactant solutions to a value close to 7. It was decided to proceed with this change since the adsorption behaviour of these surfactants is recognized to be improved in a medium with higher pH [68].

The qualitative results revealed that the effectiveness of the dispersions appeared to improve when the pH of the surfactant solutions was changed to around 7. Particularly, the surfactants Amber 2012 and Amber 2014 proved to be greatly affected by this parameter, as is depicted in Figure 4.1, in which a dispersion of MWCNTs using Amber 2012 with (Figure 4.1b) and without (Figure 4.1a) a change of its pH are shown. In all cases, a change of ultrasound time from 5 to 10 minutes appeared to either improve or keep a good MWCNTs dispersion.

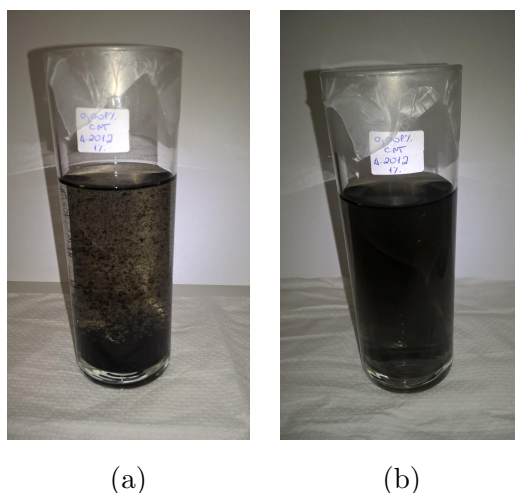


Figure 4.1: Dispersion of 0.001% MWCNTs using 1% Amber 2012: a) without pH modification; b) with a change in the pH to a value close to 7.

Considering these preliminary results, and in order to be able to make a reliable comparison between the performance of the different surfactants, the final conditions chosen to assess the particle size distribution in the ZNS equipment were: surfactant concentrations of 0.1% and 1%, applying 10 minutes of ultrasounds and modifying the pH of the surfactant solution to a value close to 7. These conditions were also the ones used to test the remaining surfactants mentioned at the beginning of this chapter. The results obtained for the hydrodynamic diameter measurements (D_z) are presented in Table 4.1 (for both surfactant concentrations tested, 1% and 0.1%), corresponding to the size distribution curves presented in Appendix F .

According to the data obtained, it is clear that a concentration of 0.1% of surfactant promotes a better dispersion of the MWCNTs than a concentration of 1%, for all of the surfactants tested. This behaviour may be explained by two hypothesis. First, the ad-

dition of a higher amount of surfactant may lead to the formation of micelles, i.e., the surfactant molecules, having more affinity to each other than to the aqueous media, will arrange themselves into small aggregates, rather than adsorbing onto the CNTs surface (the concentration at which this process starts to occur is called critical micelle concentration - cmc). However, these structures can also act as a protective shield, contributing to the dispersion of hydrophobic particles in the aqueous phase. Knowing this, it is not sure whether this mechanism contributes to the tendency described before [68]. Second, if the surfactant molecules are large enough, another phenomenon can take place, namely flocculation by bridging. This happens when the surfactant molecules adsorbed onto the nanoparticle surface extend into the liquid medium, making it possible for the extended portions to interact with each other, hence promoting flocculation instead of dispersion [68].

It is worth noting that no pH change was carried out when using Pluronic F-127, neither for the surfactant mixtures, due to the fact that both Pluronic F-127 and Glycerol are non-ionic surfactants, hence their adsorption properties are not significantly affected by a change in the pH of the medium.

As stated before, the hydrodynamic diameter measurements obtained for the dispersions containing 1% solutions of the different surfactants to disperse 0.001% MWCNTs were not within the acceptable values to be considered a suitable dispersion. Thus, only the conditions present in Table 4.1 corresponding to the surfactant concentration of 0.1% were used to prepare the dispersions that were then added to the soil/Portland cement composite.

4.2 MWCNTs applied to soil

The optimization of the MWCNTs dispersion conditions was followed by their addition to the soft soil of *Baixo Mondego* along with Portland cement, and the results regarding the assessment of the mechanical properties of the composite material are presented in this section.

The UCS tests allowed to determine the maximum unconfined compressive strength (q_{umax}) of the sample, as well as the secant undrained Young's modulus at 50% of the value of q_{umax} (E_{u50}), which expresses the stiffness of the sample. In addition, the final water content (W_f) was also measured for all samples tested, which allow to infer about the extension of the hydration reactions of Portland cement particles that occur during the curing process.

The test samples were prepared according to the UCS tests plan presented in section 3.3. For each UCS test two samples were prepared in the exact same conditions, and

Table 4.1: Characterization of MWCNTs dispersions - different surfactants at concentrations of 1% and 0.1% (MWCNTs=0.001%). In all surfactant solutions, except for Pluronic F-127 and the surfactant mixtures, the pH was modified to a value close to 7.

Surfactant	Concentration			
	1%		0.1%	
	D_z (nm)	D_z^{av} (nm)	D_z (nm)	D_z^{av} (nm)
Amber 2009	848.40		398.20	
	863.20	875.80	428.50	389.43
	915.80		341.60	
Amber 2012	*	*	305.80	
			310.00	293.90
			265.90	
Amber 2013	1330.00		414.50	
	1731.00	1444.00	373.00	384.93
	1271.00		367.30	
Amber 2014	892.30		356.70	
	750.40	858.93	359.60	346.63
	934.10		323.60	
polyDADMAC HMW	441.40		296.40	
	526.50	503.63	307.50	299.37
	543.00		294.20	
polyDADMAC MMW	1252.00		285.30	
	1326.00	1257.00	292.20	289.70
	1193.00		291.60	
Pluronic F-126	334.20		205.40	
	324.40	333.97	215.40	218.53
	343.30		234.80	
Pluronic F-127 + polyDADMAC MMW	-		271.60	
	-	-	251.70	259.87
Glycerox + polyDADMAC MMW	-		256.30	
	-		121.40	
	-	-	126.50	124.67
	-		126.10	

*Sample not tested since the presence of aggregates was clear at the naked eye.

so the final values considered for analysis correspond to the average of the two values obtained for each sample, indicated by the superscript ^{av}.

Table 4.2 displays the results obtained for the UCS reference test, i.e., without the addition of neither surfactants nor MWCNTs. The reference sample contains only soil, mixed with water (in order to keep the water content constant throughout all tests performed) and binder (Portland cement). All the other results obtained are compared with the reference test, through the calculation of their variation (indicated by the superscript ^{var}), in order to quantitatively assess the influence of the different conditions tested in the mechanical performance of the stabilized composite material.

Table 4.2: UCS tests results for the reference test.

q_{umax} (KPa)	q_{umax}^{av} (KPa)	Eu_{50} (MPa)	Eu_{50}^{av} (MPa)	W_f (%)	W_f^{av} (%)
252.36	255.08	63.56	68.45	75.07	74.98
257.79		73.33		74.88	

Table 4.3: UCS tests results for samples containing Amber surfactants, provided by aquaTECH.

Surfactant	MWCNT	q_{umax} (KPa)	q_{umax}^{av} (KPa)	q_{umax}^{var} (%)	Eu_{50} (MPa)	Eu_{50}^{av} (MPa)	Eu_{50}^{var} (%)	W_f (%)	W_f^{av} (%)
Amber 2009	-	304.44	292.66	14.73	43.28	43.55	-36.37	71.23	71.90
		280.88			43.82			72.56	
	0.001%	283.14 *	283.14	11.00	42.32 *	42.32	-38.17	72.70 *	72.70
Amber 2012	-	219.89	220.39	-13.60	41.72	40.04	-41.50	72.13	73.15
		220.89			38.36			74.16	
	0.001%	295.20	286.93	12.49	67.81	60.86	-11.08	71.56	71.11
278.65	53.90	70.65							
Amber 2013	-	260.46	258.89	1.50	26.43	32.38	-52.70	73.09	73.59
		257.33			38.32			74.08	
	0.001%	271.56	269.29	5.57	30.93	29.25	-56.24	71.55	71.51
267.02	28.98	71.46							
Amber 2014	-	248.61	240.15	-5.85	63.56	60.02	-12.31	73.05	72.36
		231.70			56.49			71.66	
	0.001%	* 250.24	250.24	-1.90	* 51.31	51.31	-25.04	* 71.34	71.34

*Result not considered due to the sample's bad quality.

Tables 4.3, 4.4 and 4.5 contain the UCS tests results for all the conditions tested. In Table 4.5, Mixture 1 refers to Pluronic F-127 with polyDADMAC MMW and Mixture 2 refers to Glycerox with polyDADMAC MMW.

Knowing that the addition of a surfactant solution by its own can have a dispersing effect on the Portland cement particles present in the stabilized soil, which cannot be discarded, UCS tests were conducted first using only the surfactant solution, without MWCNTs, and afterwards using the surfactant solution containing MWCNTs.

Table 4.4: UCS tests results for samples containing surfactants acquired from Sigma-Aldrich.

Surfactant	MWCNT	q_{umax} (KPa)	q_{umax}^{av} (KPa)	q_{umax}^{var} (%)	Eu_{50} (MPa)	Eu_{50}^{av} (MPa)	Eu_{50}^{var} (%)	W_f (%)	W_f^{av} (%)
HMW 0.1%	-	235.57	230.37	-9.69	39.64	37.41	-45.34	71.07	70.95
		225.17			35.18			70.82	
	0.001%	222.05	230.18	-9.76	47.82	41.58	-39.24	72.06	71.67
		238.32			35.35			71.28	
MMW 0.1%	-	*	262.20	2.79	*	58.95	-13.87	*	72.65
		262.20			58.95			72.65	
	0.001%	258.14	262.35	2.85	53.32	57.85	-15.48	71.72	71.88
		266.55			62.37			72.04	
Pluronic F-127 0.1%	-	266.82	271.11	6.28	58.18	55.75	-18.54	72.76	72.33
		275.39			53.33			71.90	
	0.001%	251.43	251.44	-1.43	40.73	47.50	-30.60	71.14	71.92
		251.45			54.27			72.70	

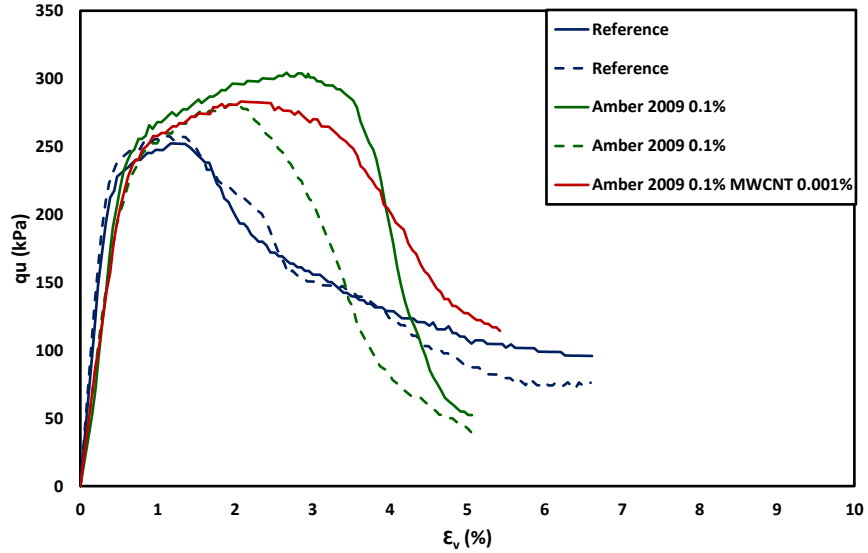
*Result not considered due to the sample's bad quality.

Table 4.5: UCS test results for samples containing a mixture of surfactants.

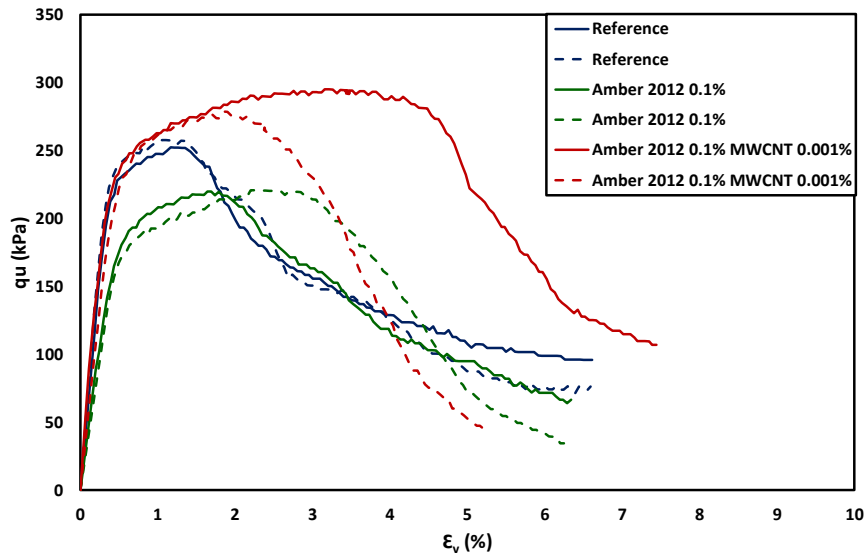
Surfactant	MWCNT	q_{umax} (KPa)	q_{umax}^{av} (KPa)	q_{umax}^{var} (%)	Eu_{50} (MPa)	Eu_{50}^{av} (MPa)	Eu_{50}^{var} (%)	W_f (%)	W_f^{av} (%)
Mixture 1 0.1%	-	233.94	246.90	-3.21	36.21	33.34	-51.28	73.10	72.88
		259.86			30.47			72.65	
	0.001%	254.85	271.63	6.49	61.14	59.46	-13.13	72.51	72.25
		288.41			57.78			71.98	
Mixture 2 0.1%	-	234.33	247.13	-3.12	34.92	34.72	-49.27	71.54	71.90
		259.92			34.52			72.26	
	0.001%	266.33	256.72	0.64	57.14	53.23	-22.23	72.76	72.65
		247.11			49.32			72.53	

Looking at these three tables, it can be noted that in all cases there is a negative effect

of the addition of either surfactant only or surfactant with MWCNTs in the value of E_{u50} , meaning that all the soil composites tested have a stiffness lower than the reference test. Materials with lower stiffness will exhibit higher strains for the same stress level, which is why this effect can come as an advantage for civil engineering applications.



(a)



(b)

Figure 4.2: Stress-strain plots obtained from UCS tests of samples containing : a) Amber 2009; b) Amber 2012.

In the case of samples containing MWCNTs, this effect can be explained based on their properties - these particles are very strong and ductile, which means that they can withstand high strains at failure, providing the composite material with a more ductile behaviour [28]. For the samples containing only surfactant, the explanation for the de-

crease in Eu_{50} relative to the reference test may rely on the fact that surfactant molecules can act as a plasticizer agent, capable of dispersing Portland cement particles and other constituent particles of the soil, by adsorption at their surface, making this material more fluid and thus contributing to a lower stiffness [69].

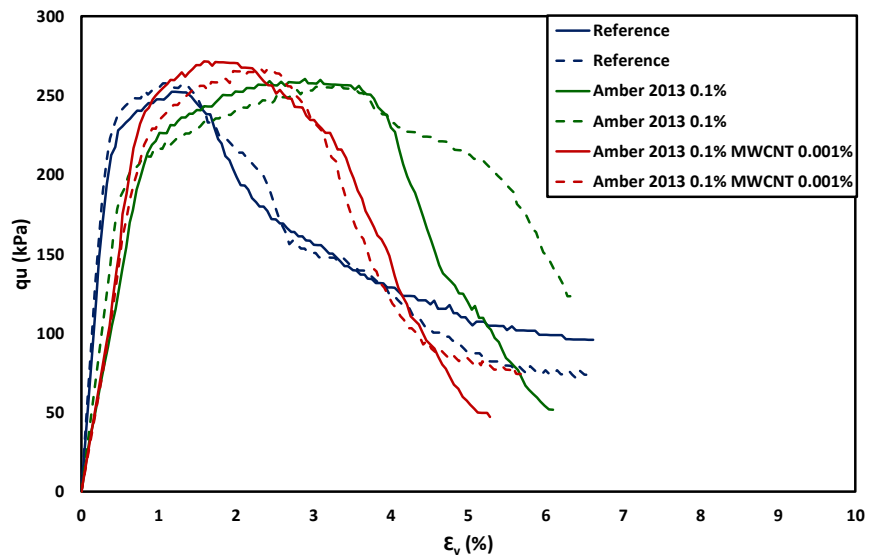
The most important parameter used to assess the effectiveness of the chemically stabilized soil in terms of mechanical behaviour is the q_{umax} . The next paragraphs contain an analysis of the mechanical behaviour of the different samples based on this parameter. Additionally, stress-strain plots ($q_{umax}-\varepsilon$) were built in order to better understand the sample's behaviour during the UCS test.

Among all the tests conducted, there are two conditions tested with unexpected results, more specifically the tests conducted with the addition of Pluronic F-127 only versus Pluronic F-127 enriched with MWCNTs (Table 4.4). In this case, the addition of MWCNTs shows a negative effect in the sample's compression strength. In theory, there should be no reason for this to occur, knowing that there is an improvement of the sample strength relative to the reference when Pluronic F-127 only is added, and MWCNTs should not be responsible for such a negative effect in the mechanical strength. One possible explanation for such results is that there could have been a problem with this test, occurred during the sample preparation, curing and/or the UCS measurement. Therefore, these results require future validation before being considered.

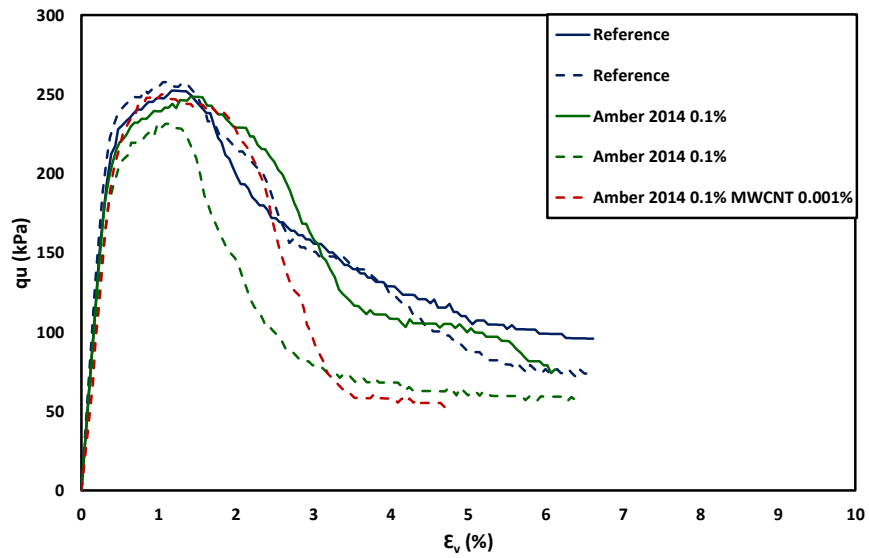
In respect to the composite samples tested with polyDADMAC surfactants, both the ones provided by aquaTECH (Table 4.3) and the ones acquired from Sigma-Aldrich (Table 4.4), several aspects can be pointed out. From Table 4.3, it is distinctly visible that the addition of Amber 2014 to the soil, either with or without MWCNTs, had a negative influence in the mechanical strength of the sample compared to reference test (showing variations of -1.90% and -5.85%, respectively), while Amber 2009, with and without MWCNTs, and Amber 2012 with MWCNTs yielded interesting improvements relative to the reference test (showing variations of 11.00%, 14.73% and 12.49%, respectively). The use of Amber 2013, with and without MWCNTs, also resulted in a mechanical strength improvement, but of lower magnitude (in these cases the variation was of 5.57% and 1.50%, respectively).

A deeper analysis of Table 4.3 and Figures 4.2 and 4.3 (where the stress-strain plots for the UCS tests containing the Amber surfactants are shown) leads to the conclusion that for all samples containing Amber surfactants enriched with MWCNTs there was an increase in the value of q_{umax} when compared to the samples containing surfactant only (which is in good agreement with what was expected to happen), except for the case of Amber 2009, in which the q_{umax} value for the sample with MWCNTs is slightly lower than the one obtained for the sample containing surfactant only (however this result is

within the experimental variability).



(a)



(b)

Figure 4.3: Stress-strain plots obtained from UCS tests of samples containing : a) Amber 2013; b) Amber 2014.

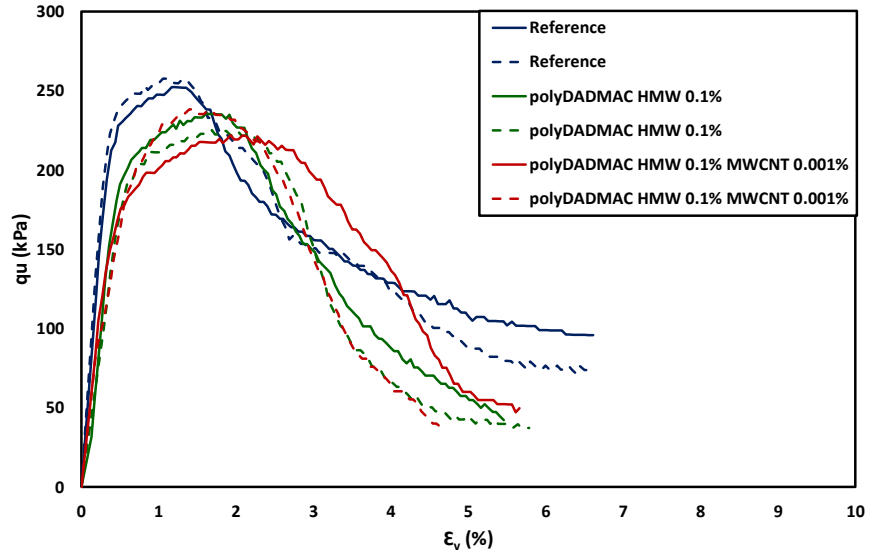
As was mentioned previously, polyDADMAC surfactants (cationic in nature), exhibit a better performance in mediums with higher pH. After the cement hydration reactions occur, the pH of the composite material reaches values around 12; however the pH of the soil by its own is acid (in fact, the pH of the soil used to conduct this experimental work was measured and a value of 5.34 was obtained). It is possible that the polyDADMAC surfactants (which include the Ambers and the polyDADMACs from Sigma) could be affected by the pH at an initial stage of the curing process, when the cement reactions have

not yet started to raise the pH of the composite medium, leading to their degradation or loss of their functionality, which is then reflected in lower improvements (or in some cases, even losses) of mechanical strength of the composite materials, namely with MWCNTs, relative to the reference test. The degree of dispersion of the MWCNTs may be worse in the soil than in the preliminary tests used to evaluate the nanotubes dispersion.

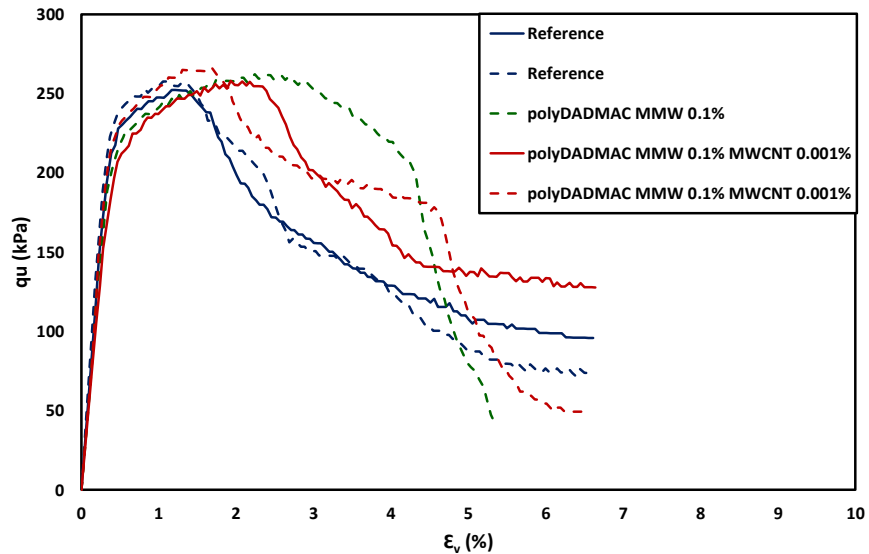
It is important to keep in mind that the properties of the medium (soil) to which the MWCNTs dispersions were added have a huge influence on the stabilizing behaviour. This explains why some of the surfactants that worked very well on MWCNTs dispersions performed poorly when added to the soil/Portland cement composite. The effect of the medium is fairly evident when the samples containing Amber 2012 or polyDADMAC MMW, both enriched with MWCNTs, are compared. When assessing the quality of the MWCNTs dispersions through the DLS technique, the D_z values obtained using 0.1% Amber 2012 or 0.1% of polyDADMAC MMW were very close (293.9 nm and 289.7 nm, respectively - see Table 4.1), as was expected since these molecules had similar size and molecular weight (see Table 3.5). In spite of this, when these dispersions were added to the soil composite, the samples exhibited very distinct mechanical behaviours - the composite material containing Amber 2012 with MWCNTs showed an improvement of 12.49% of q_{umax} , while for the composite material containing polyDADMAC MMW with MWCNTs this improvement was only of 2.85% (relative to the reference test). Additionally, the influence of the medium is well expressed by the result of the sample containing the mixture of Glycerox with polyDADMAC MMW. In this case, even though the result of the MWCNTs dispersion is the best one obtained (with a D_z of 124.67 nm -Table 4.1), the UCS performance test resulted in an insignificant mechanical strength improvement relative to the reference test (only 0.64% - see Table 4.5).

Concerning the tests performed with the polyDADMAC HMW and polyDADMAC MMW (Table 4.4 and Figure 4.4), there is no visible improvements resulting from the addition of MWCNTs relative to the test where surfactant only is added to the soil/Portland cement composite. However, there is a considerable difference between the mechanical performance of the composites containing these two surfactants - when using either polyDADMAC HMW only or polyDADMAC HMW/MWCNTs, there is a loss of mechanical strength of the sample compared to the reference (-9.69% and -9.76%, respectively), whereas when using either polyDADMAC MMW only or polyDADMAC MMW/MWCNTs a slight improvement on the mechanical strength of the sample is observed (2.79% and 2.85%, respectively). If the data provided by the supplier regarding the molecular weight of these surfactants is considered as accurate (400-500 kDa for polyDADMAC HMW and 200-350 kDa for polyDADMAC MMW), then the results described above can be explained by the fact that the surfactant with higher molecular weight (poly-

DADMAC HMW), can potentially cause a delay of the hydration reactions of the cement particles, which results in lower compression strength values.



(a)

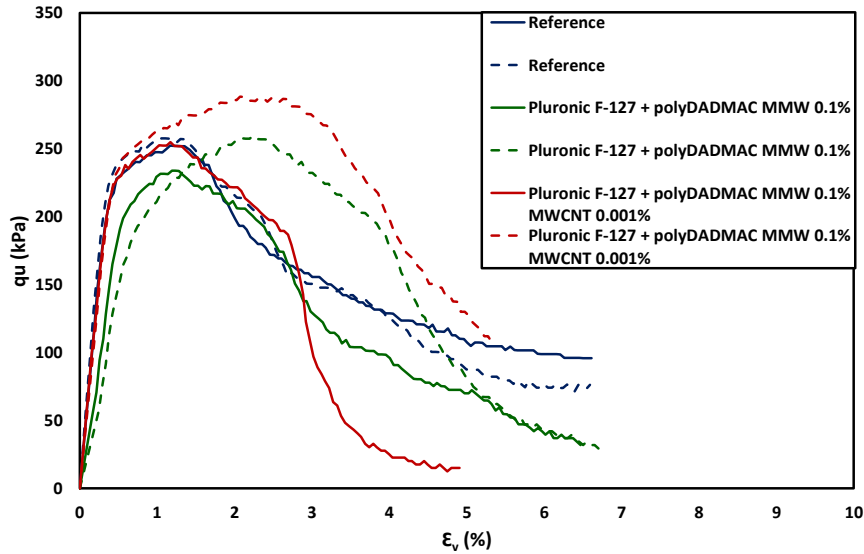


(b)

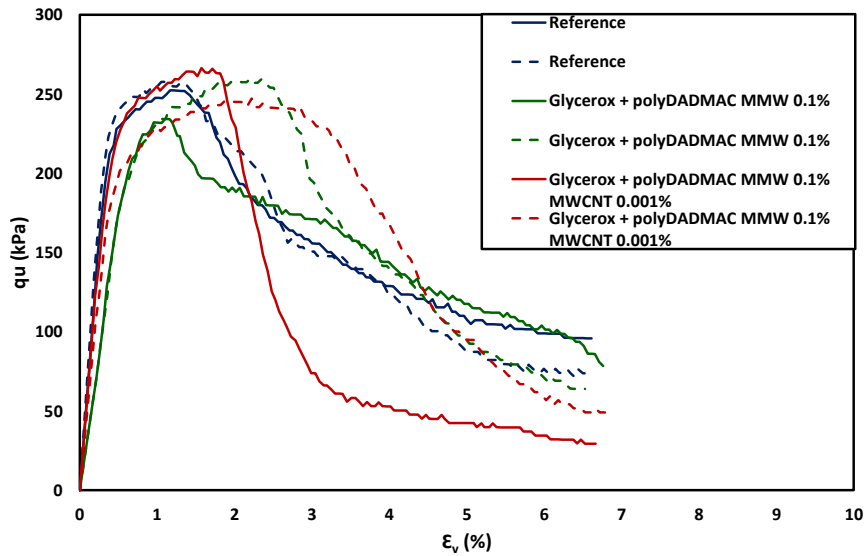
Figure 4.4: Stress-strain plots obtained from UCS tests of samples containing : a) polyDADMAC HMW; b) polyDADMAC MMW.

Regarding the performance of the composite materials chemically stabilized with a mixture of surfactants (Table 4.5 and Figure 4.5), it is clear that the Pluronic F-127/polyDADMAC MMW/MWCNTs mixture was much more beneficial to the mechanical strength of the final composite material (showing an improvement of 6.49% of q_{umax}) than the Glycerox/polyDADMAC MMW/MWCNTs mixture (showing an improvement of only 0.64% of q_{umax}), even though the latter could better disperse the MWCNTs, according to

the particle size distribution results shown in Table 4.1. This discrepancy is most likely explained by the fact that Pluronic F-127, being a much smaller molecule than Glycerox (see Table 3.5), will not hinder the cement hydration reactions as much as Glycerox might. Also, looking at the size distribution for the dispersion of MWCNTs in the mixture Glycerox/PolyDADMAC MMW (Figure F.5, Appendix F), it is clear the presence of MWCNTs aggregates.



(a)



(b)

Figure 4.5: Stress-strain plots obtained from UCS tests of samples containing : a) Pluronic F-127 with polyDADMAC MMW; b) Glycerox with polyDADMAC MMW.

At the beginning of this research work it was expected, in theory, that the addition of well-dispersed MWCNTs to the soil/Portland cement composite would lead to high

mechanical improvements of the final composite materials.

The results obtained showed that for most of the samples there is a mechanical improvement due to the addition of MWCNTs, however the degree of improvement fell very away from what was expected. One possible explanation for such results is that the surfactant molecules may be covering the majority of the MWCNTs surface, thus preventing bond formation between MWCNTs and the particles present in the soil, which evidently has an unfavourable effect in the nanoreinforcement action of the MWCNTs in the final composite material [19].

Chapter 5

Conclusions and Future works

5.1 Conclusions

The main purpose of this work was to evaluate the mechanical performance of the soft soil of *Baixo Mondego* chemically stabilized and enriched with MWCNTs. In this chapter, the main conclusions withdrawn from the experimental work developed throughout this thesis are exposed.

Regarding the MWCNTs dispersions in aqueous media, it was concluded that a concentration of 0.1% of surfactant is more effective for dispersing 0.001% of MWCNTs than a concentration of 1%, for all the surfactants tested. The ultrasound time and pH revealed to be important variables in the optimization of the MWCNTs dispersions.

The addition of these dispersions to the soil, along with Portland cement, showed that in general the MWCNTs have a positive effect on the compressive strength when compared to the samples containing surfactant only; however, when compared to the reference test (which has neither surfactant nor MWCNTs) the enhancement on this mechanical property reveals to be either inefficient (in the cases where the composite samples presented values of q_{umax} lower than the reference test) or not very satisfactory (the magnitude of the q_{umax} improvement was relatively small when compared with the reference test).

The scope of this research included the use of surfactant mixtures, which may be a viable solution for the chemical stabilization of the soil containing MWCNTs. In this work, the mixture of Pluronic F-127 with polyDADMAC MMW, at a concentration of 0.1% with 0.001% MWCNTs resulted in an improvement of q_{umax} of 6.49% relative to the reference test. However, the other surfactant mixture tested (Glycerox with polyDADMAC MMW, at a concentration of 0.1% with 0.001% MWCNTs) did not perform so well, showing a negligible improvement of q_{umax} (only 0.64%). This mixture involves much larger molecules, in general, than the first one, since both polymers have a high molecular weight. It should be pointed out that the mixture of surfactants was not very explored in this work, and further tests with different surfactants at different ratios and concentrations are necessary to better understand their stabilizing behaviour in the soil.

Concerning the stiffness of the samples evaluated through the values of Eu_{50} , in all cases a decrease compared to the reference value was observed, meaning that the chemically stabilized composite material acquired a more ductile behaviour. In the case of the

samples containing surfactant only this feature is attributed to their plasticizer action in the composite material, while in the case of samples containing also MWCNTs this effect is explained by the mechanical properties of these nanoparticles as well. This is a positive result regarding applications in civil engineering.

In general, the results obtained for the mechanical properties of the composite materials studied in this work are in agreement with similar research works conducted by Casaleiro [31], Figueiredo [28] and Moura [33] (which are summarized in section 2.2), even if the mechanical improvement obtained is, in general, lower than the one obtained in those researches. The main conclusion drawn from this work is that further research is necessary to better understand the interactions between the surfactant/MWCNTs system in the soil/Portland cement medium, knowing that having a good dispersion of MWCNTs is not enough to obtain satisfactory mechanical improvements of the final soil composite material.

5.2 Future Works

Bearing in mind that this line of research is very recent, there are still many variables to be investigated. Some suggestions for future works in this area are presented below:

- It is very important to assess the effect of the initial pH of the soil on the possible degradation of the surfactants used;
- Different types of surfactants should be tested, both cationic and non-ionic, with different architectures, to verify if the MWCNTs dispersions can be further improved;
- The mixture of a cationic and non-ionic surfactant should continue to be explored, by testing different surfactant mixtures, at different ratios and concentrations, in order to analyse its influence in both the dispersion quality of MWCNTs and in the mechanical enhancement of the soil composite material;
- The mixture of a cationic and anionic surfactant could also be an interesting approach, in order to better understand the behaviour of the surfactant system when placed in the soil medium;
- It would also be of great interest to evaluate the effect of a higher concentration of MWCNTs, as well as different concentrations of surfactants and longer curing times in the mechanical properties of the chemically stabilized composite material.

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Appendix A

Granulometric curve

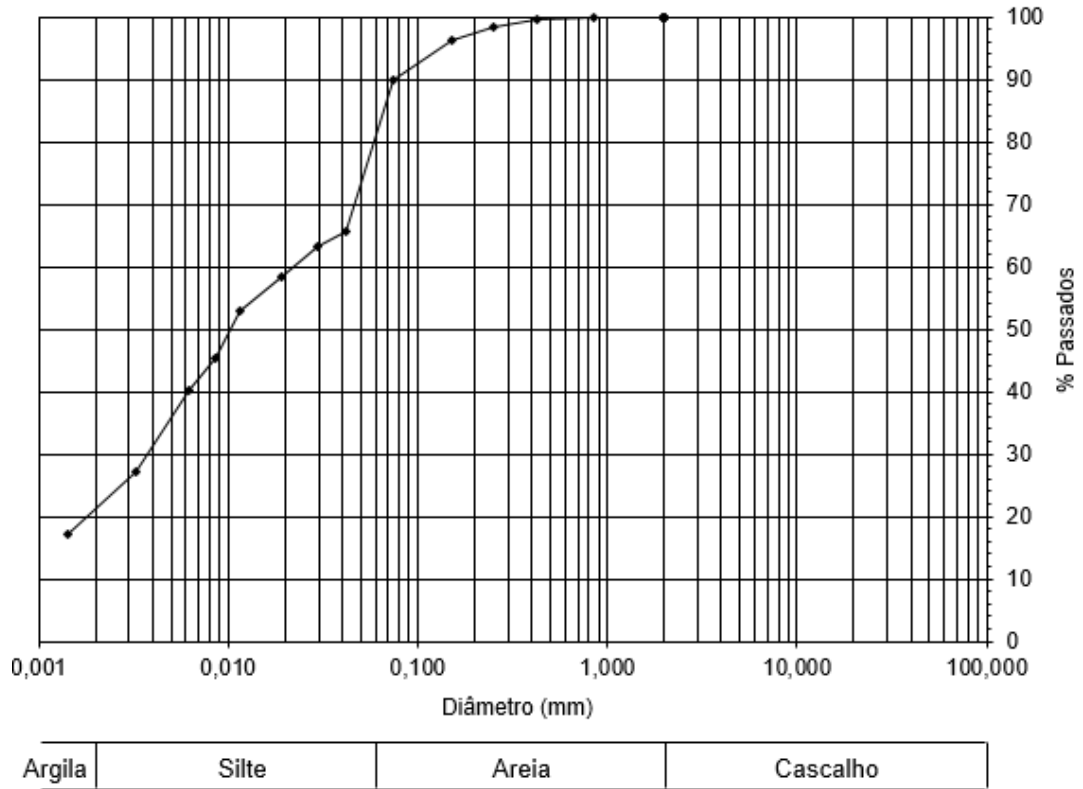
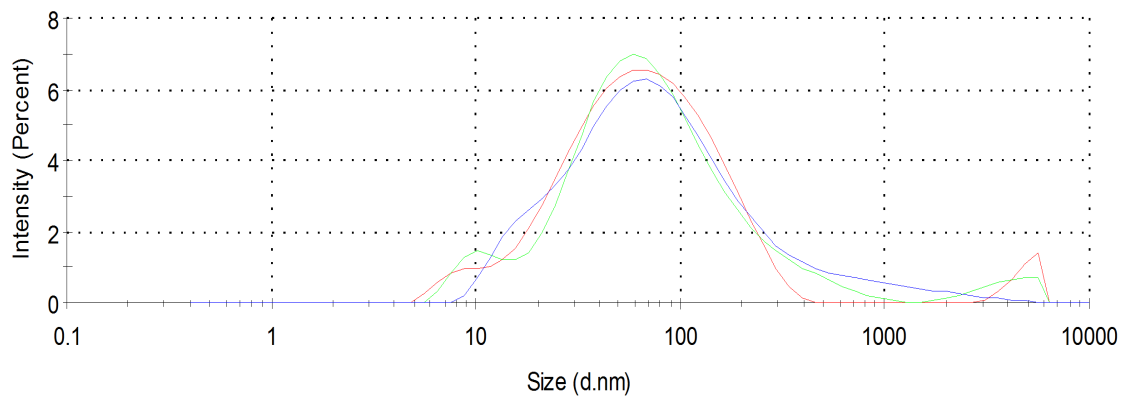


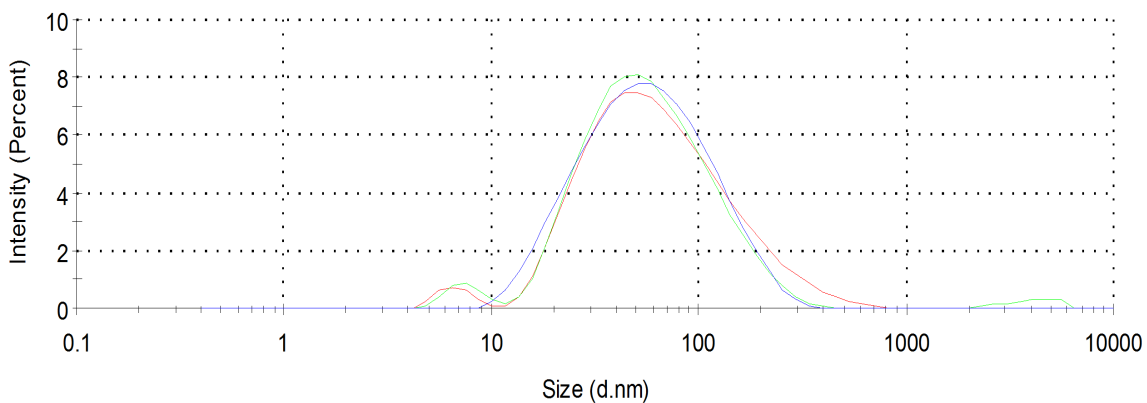
Figure A.1: Granulometric curve of the soil.

Appendix B

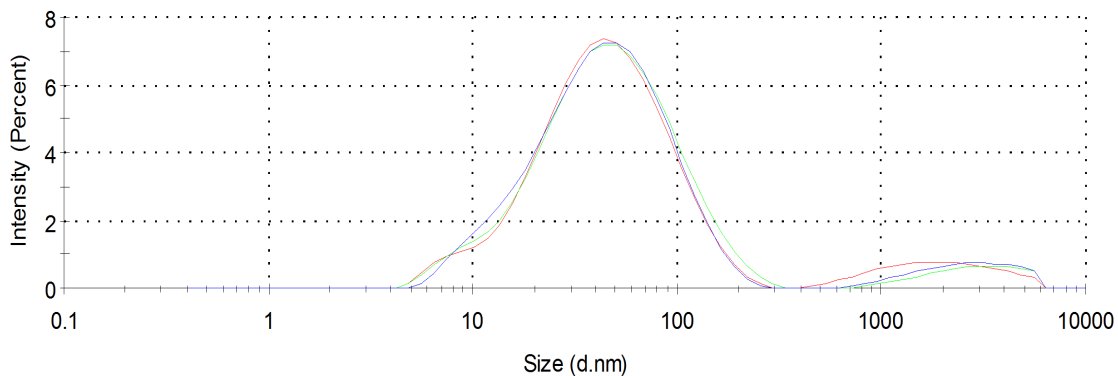
Size distribution by intensity of the surfactants



(a)

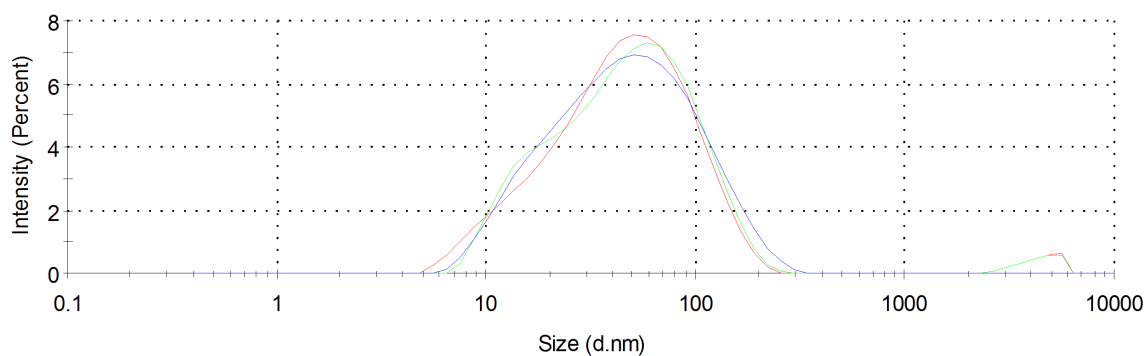


(b)

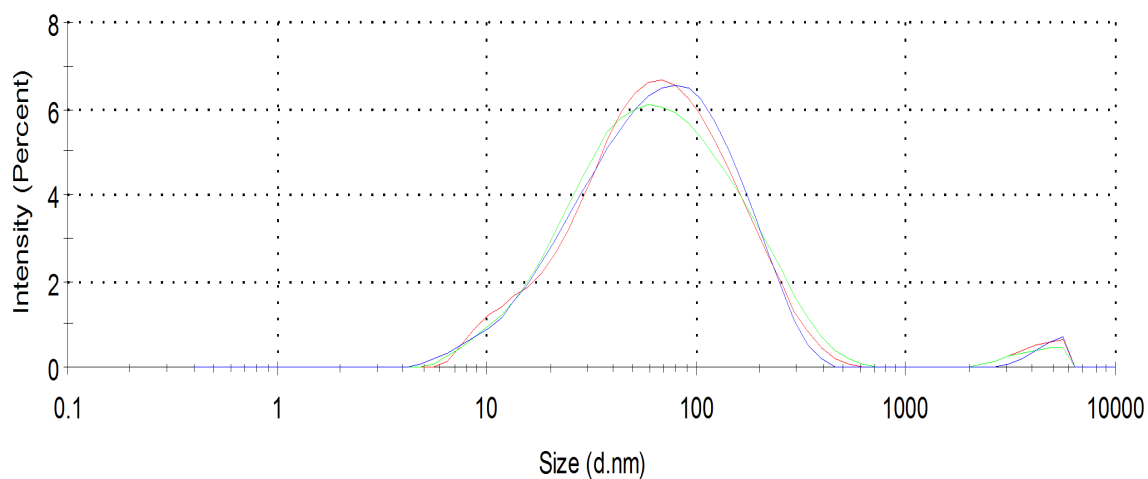


(c)

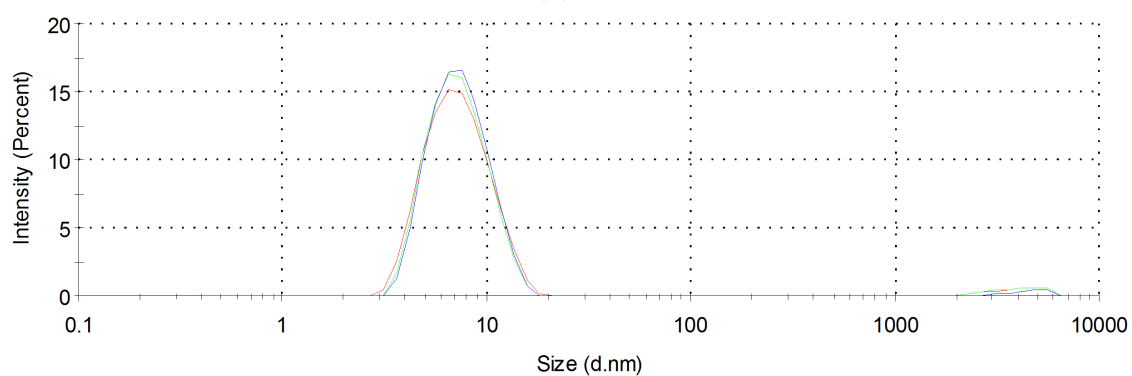
Figure B.1: Size distribution by intensity for: a) Amber 2012; b) Amber 2013; c) Amber 2014.



(a)



(b)

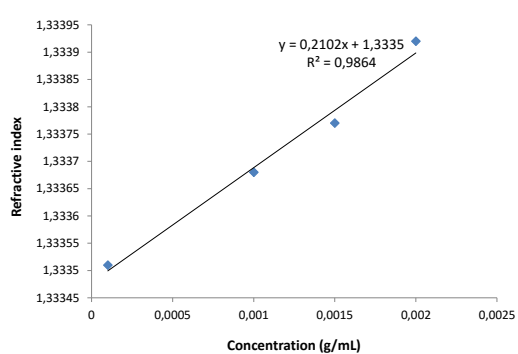


(c)

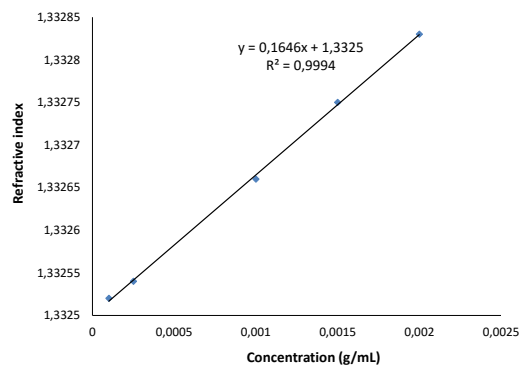
Figure B.2: Size distribution by intensity for: a) polyDADMAC HMW; b) polyDADMAC MMW; c) Pluronic F-127.

Appendix C

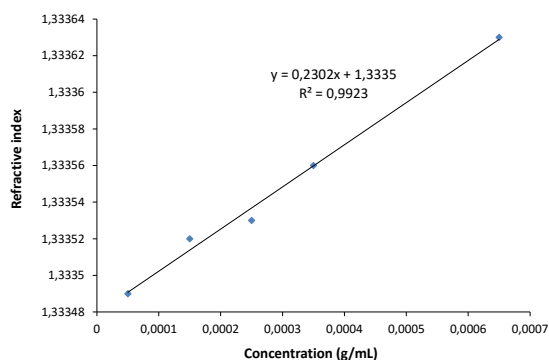
Determination of the differential refractive index increment (dn/dc)



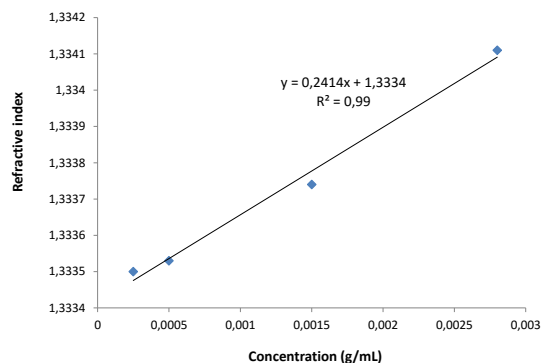
(a)



(b)



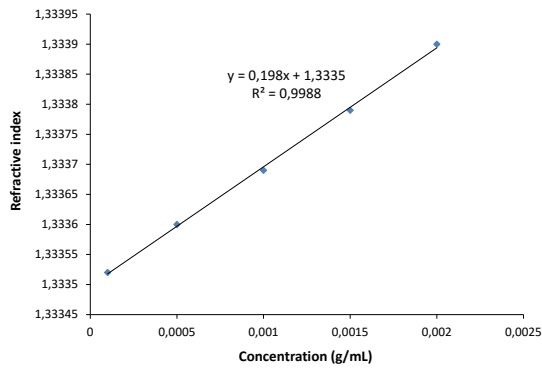
(c)



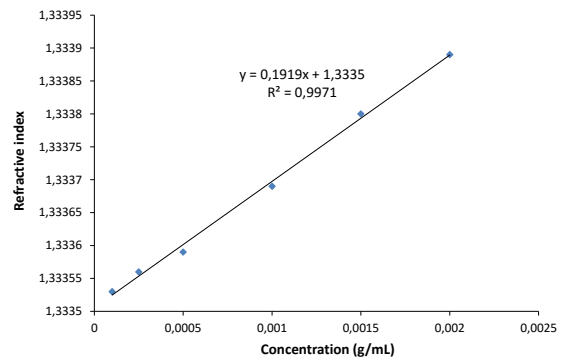
(d)

Figure C.1: Determination of the dn/dc value for: a) Amber 2009; b) Amber 2012; c) Amber 2013; d) Amber 2014.

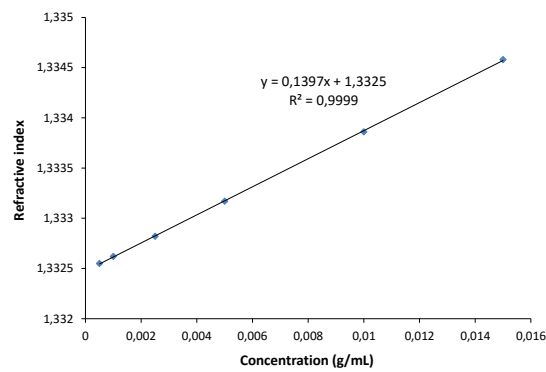
APPENDIX C. DETERMINATION OF THE DIFFERENTIAL REFRACTIVE INDEX INCREMENT (DN/DC)



(a)



(b)

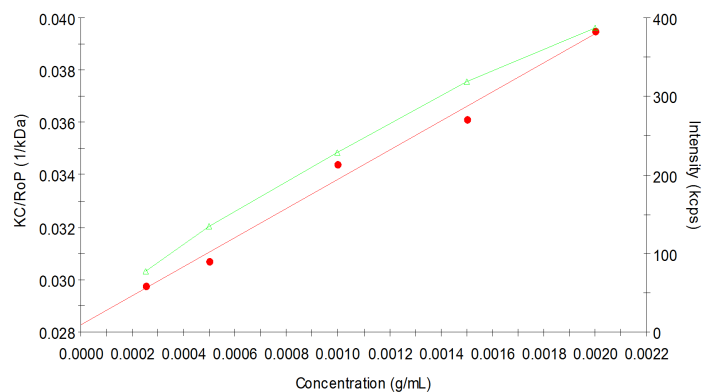


(c)

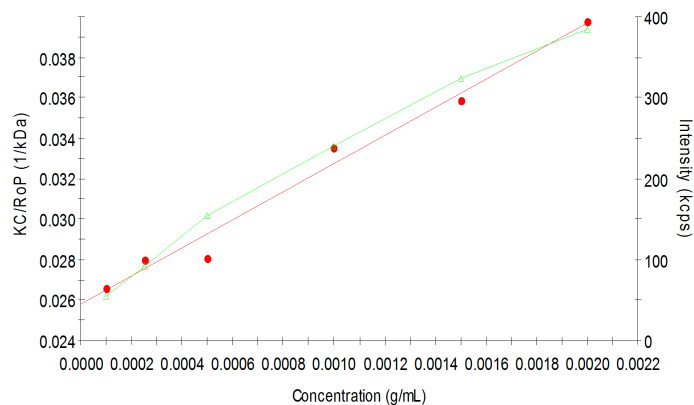
Figure C.2: Determination of the dn/dc value for: a) polyDADMAC HMW; b) polyDADMAC MMW; c) Pluronic F-127.

Appendix D

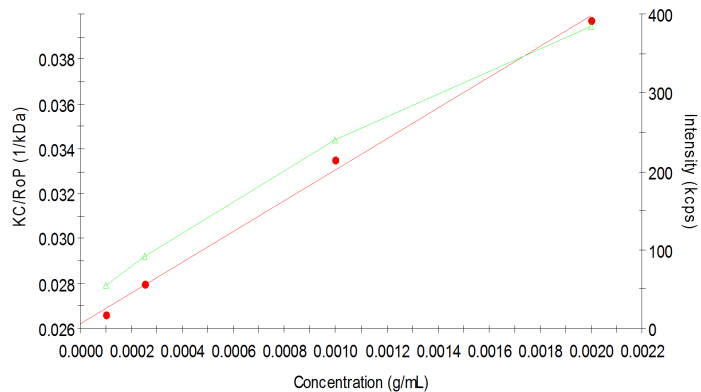
Debye plot of the surfactants



(a)

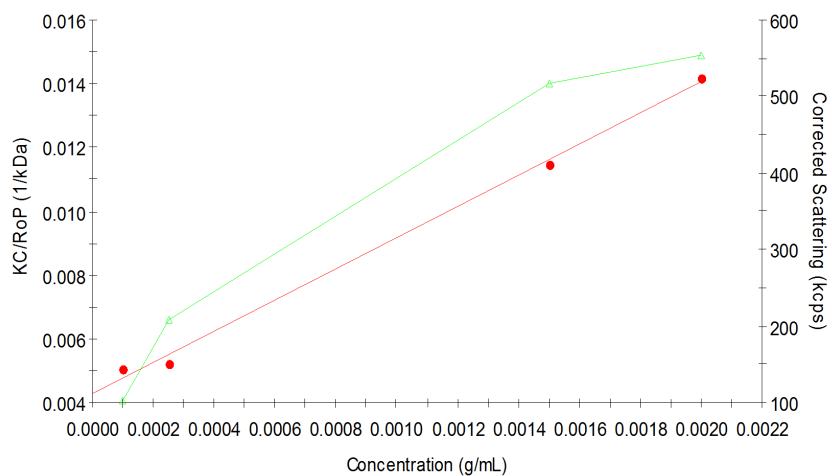


(b)

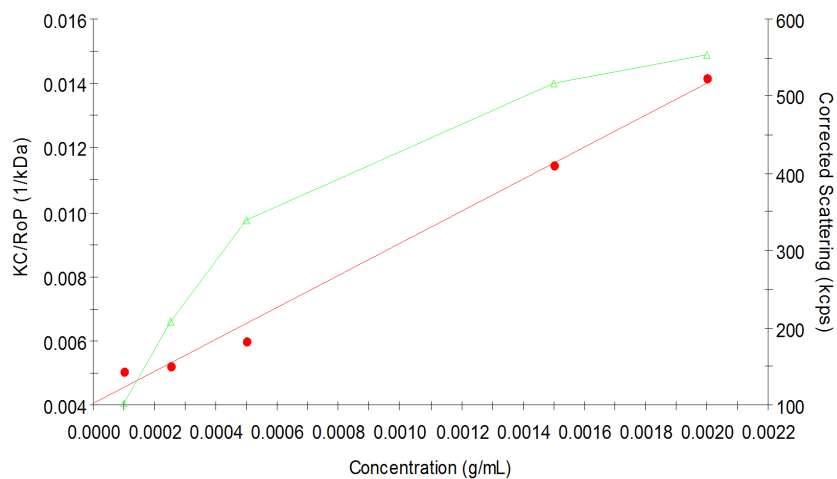


(c)

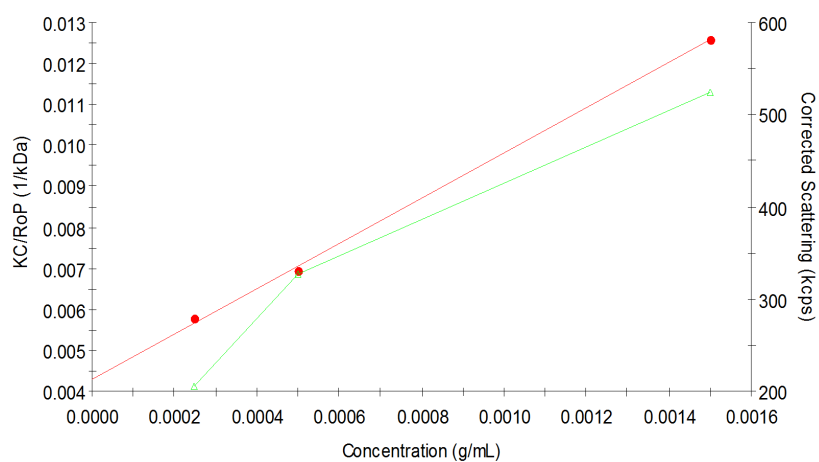
Figure D.1: Debye plot for MW determination of Amber 2009: a) first measurement; b) second measurement; c) third measurement.



(a)

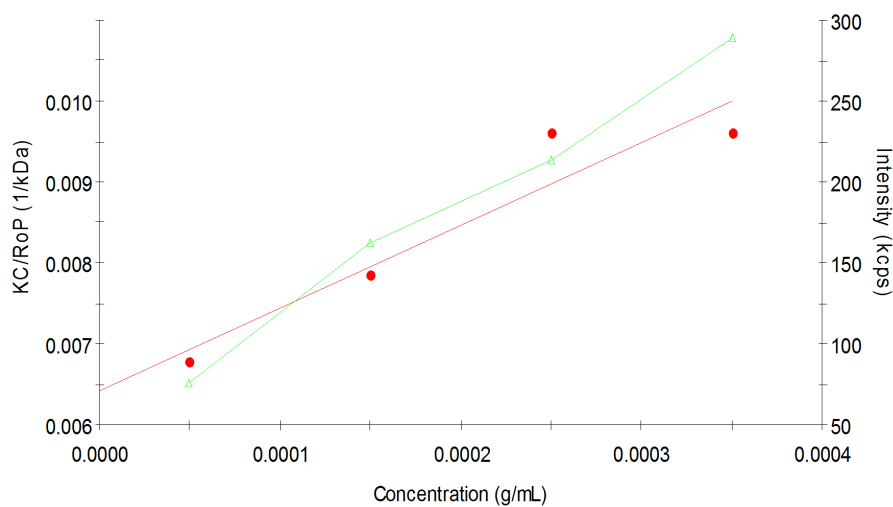


(b)

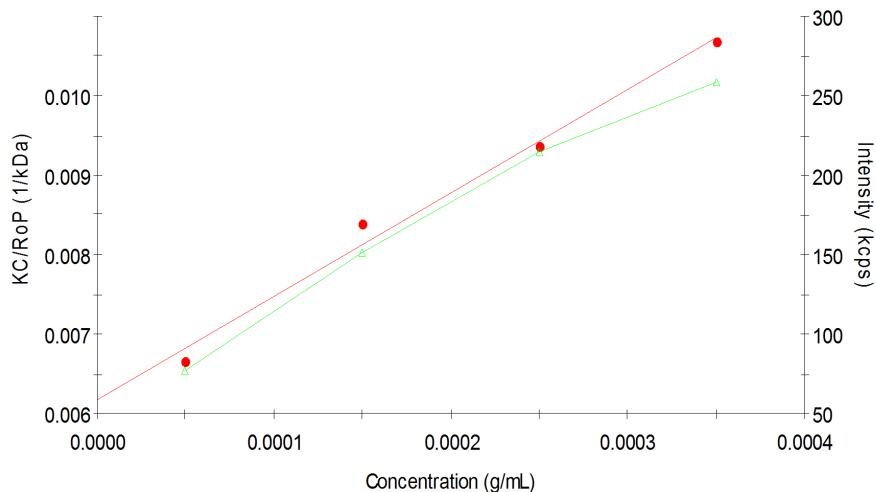


(c)

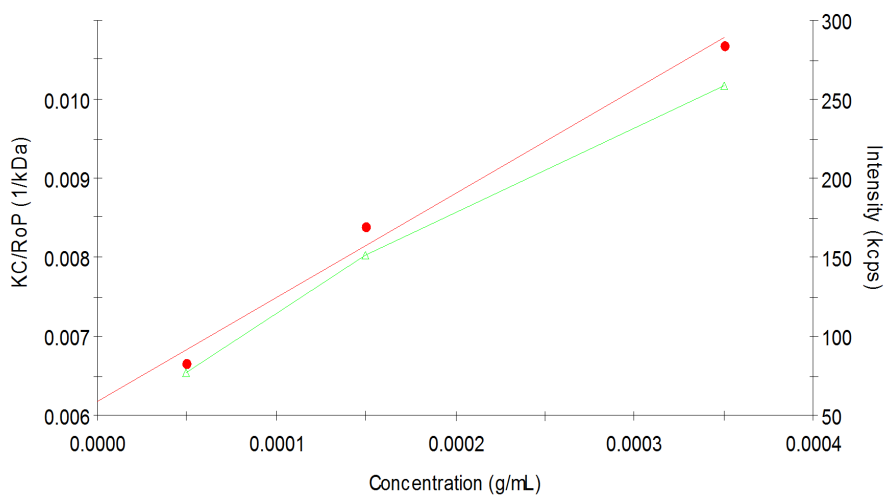
Figure D.2: Debye plot for MW determination of Amber 2012: a) first measurement; b) second measurement; c) third measurement.



(a)

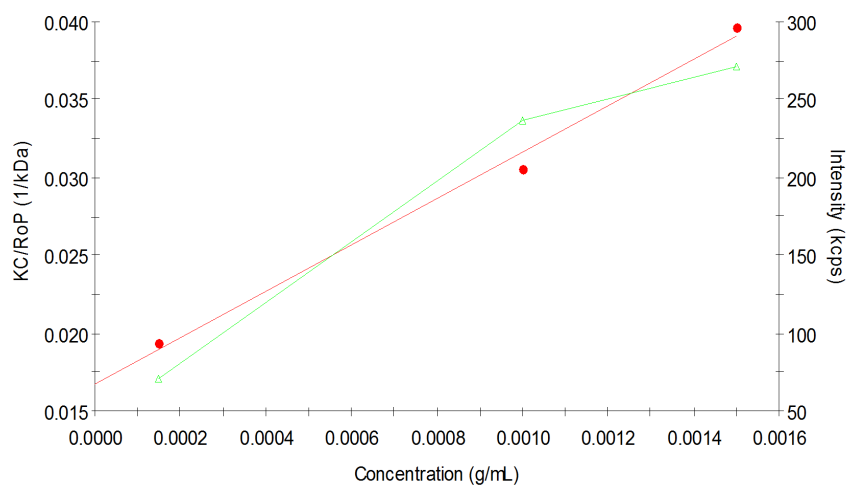


(b)

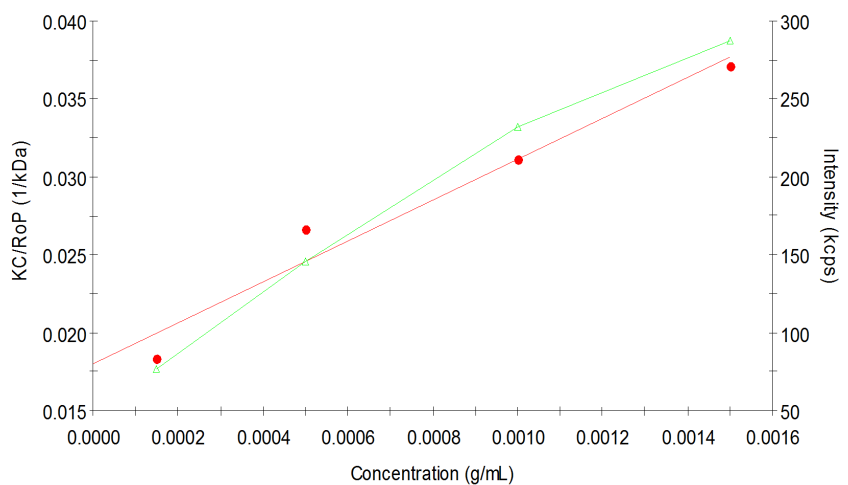


(c)

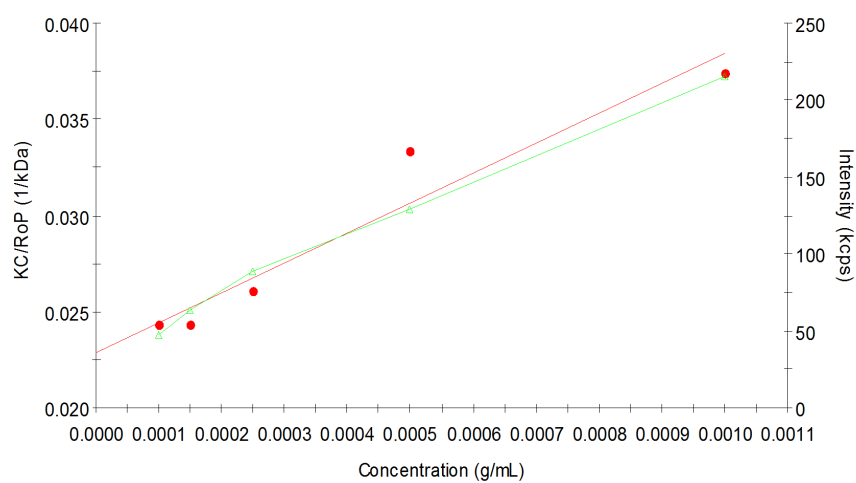
Figure D.3: Debye plot for MW determination of Amber 2013: a) first measurement; b) second measurement; c) third measurement.



(a)

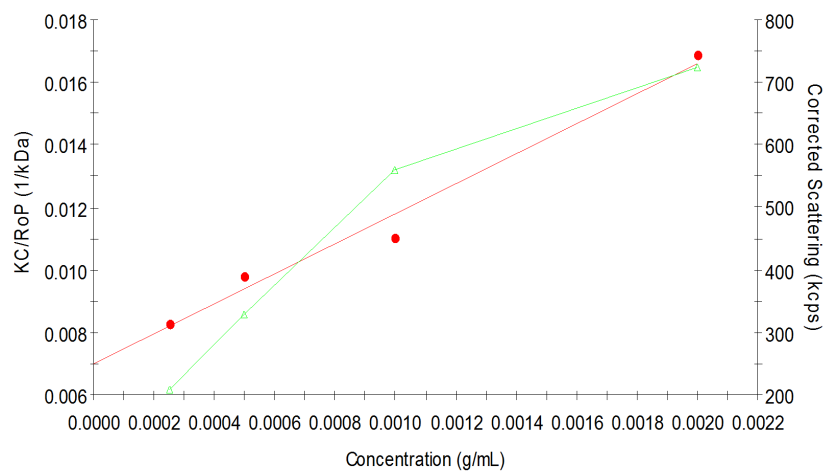


(b)

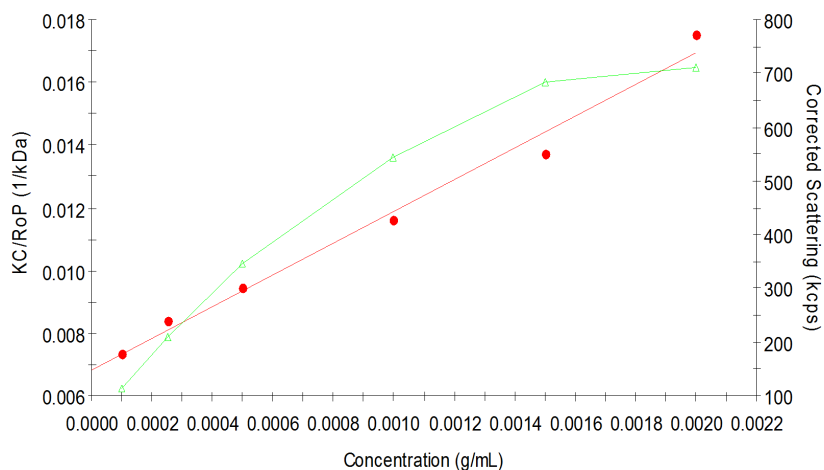


(c)

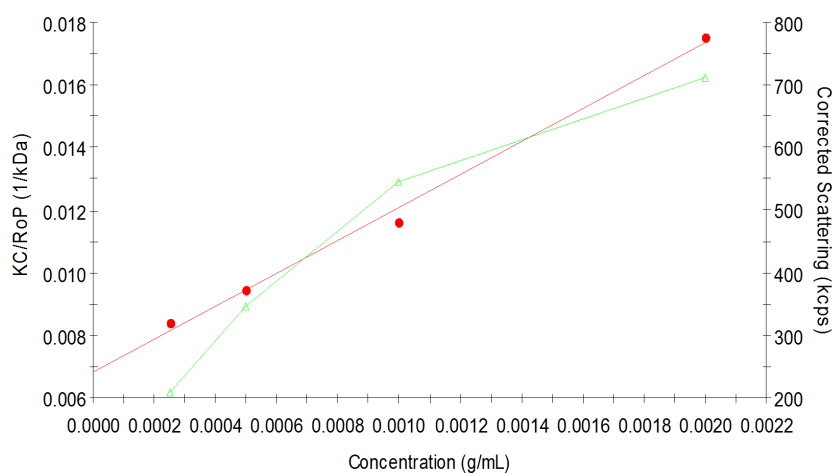
Figure D.4: Debye plot for MW determination of Amber 2014: a) first measurement; b) second measurement; c) third measurement.



(a)

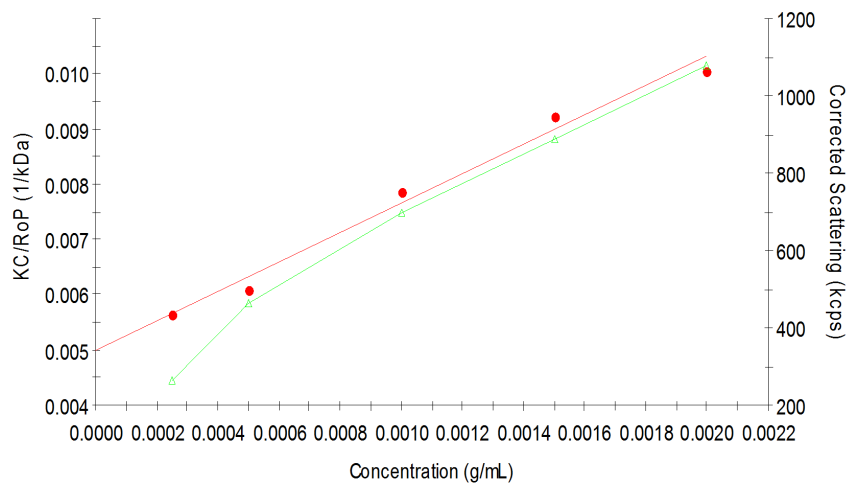


(b)

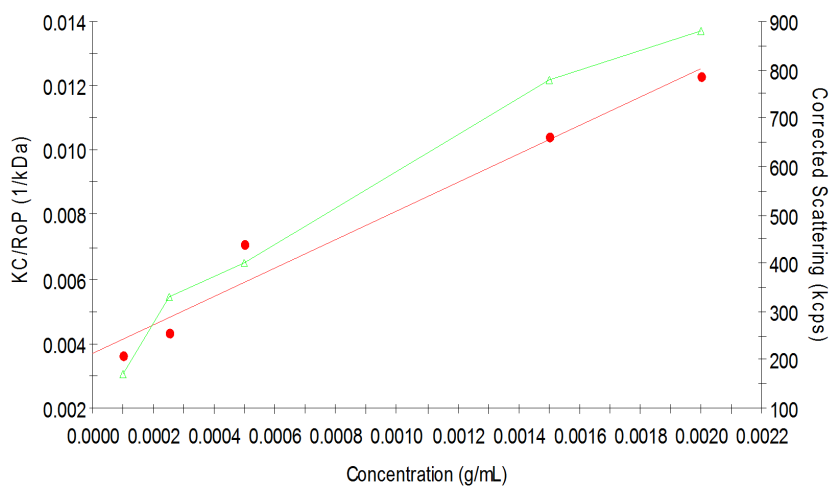


(c)

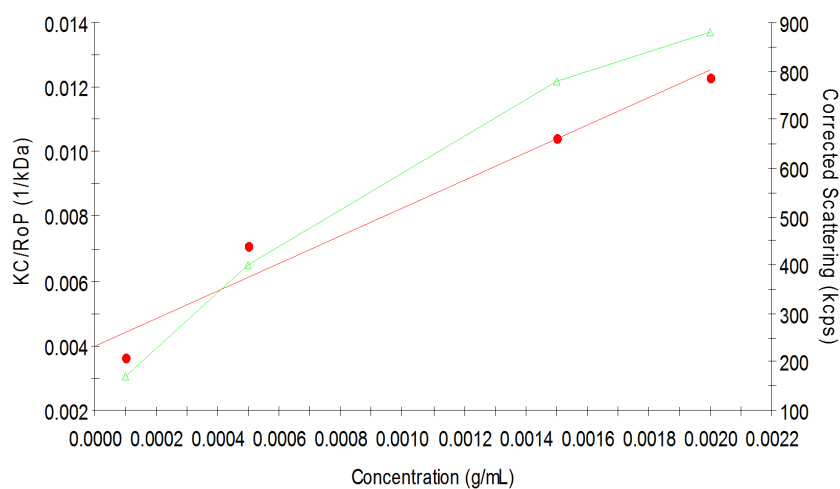
Figure D.5: Debye plot for MW determination of polyDADMAC HMW: a) first measurement; b) second measurement; c) third measurement.



(a)

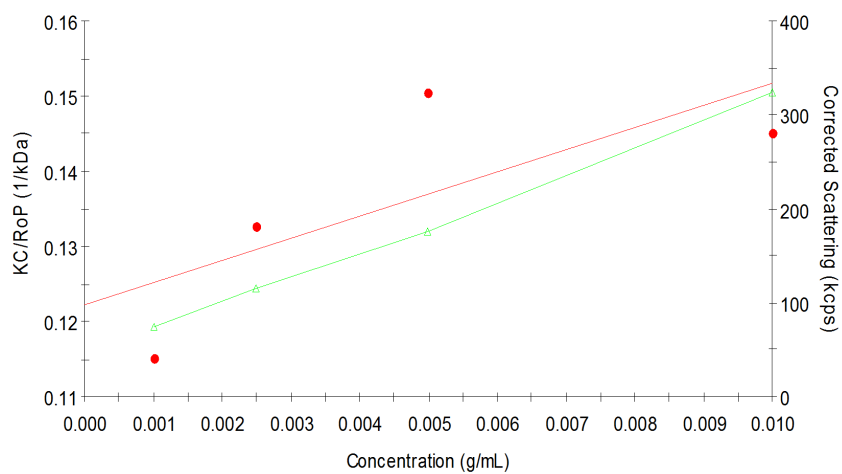


(b)

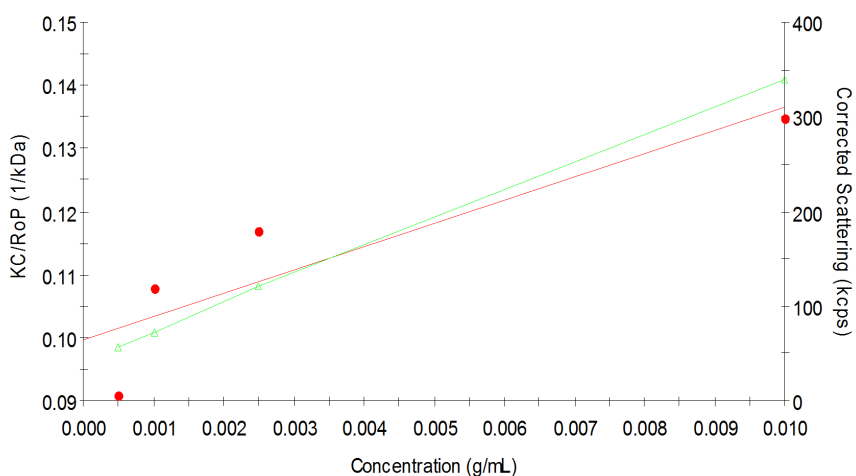


(c)

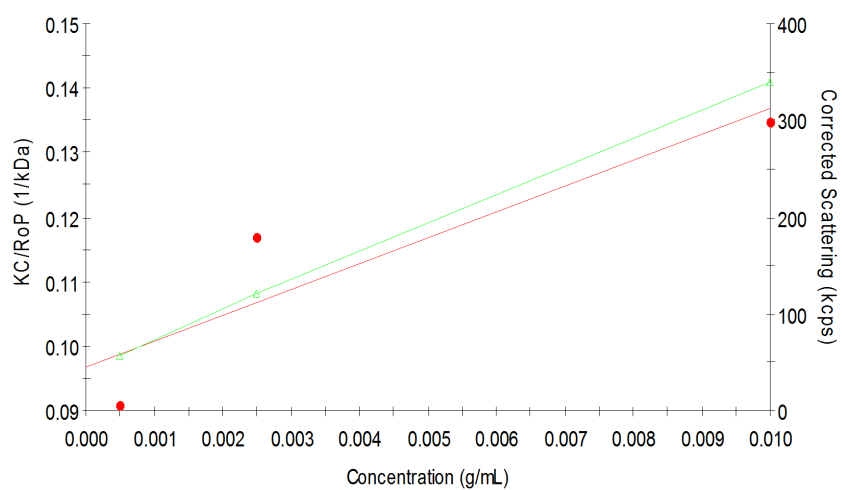
Figure D.6: Debye plot for MW determination of polyDADMAC MMW: a) first measurement; b) second measurement; c) third measurement.



(a)



(b)

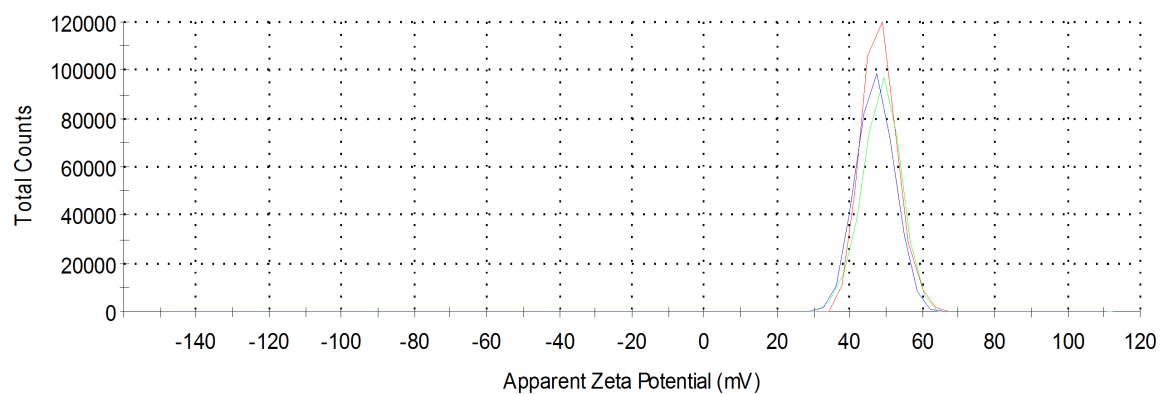


(c)

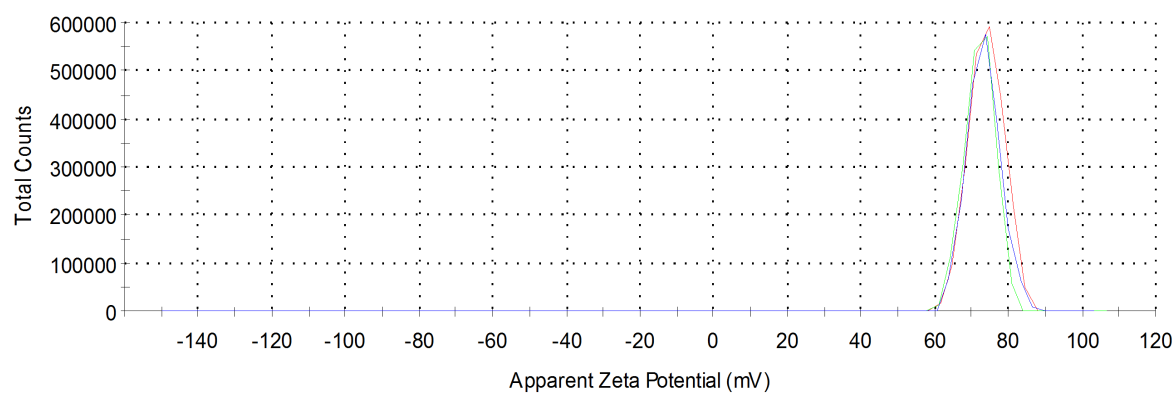
Figure D.7: Debye plot for MW determination of Pluronic F-127: a) first measurement; b) second measurement; c) third measurement.

Appendix E

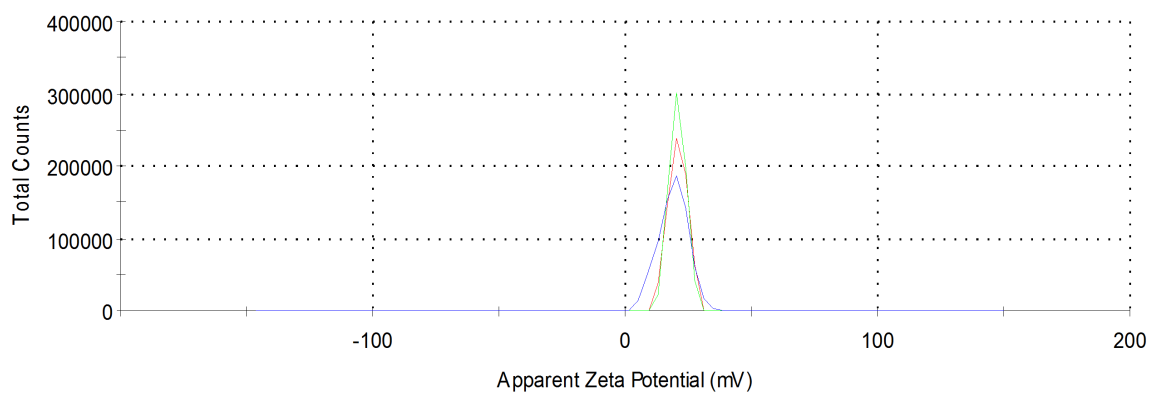
Zeta potential of the surfactants



(a)



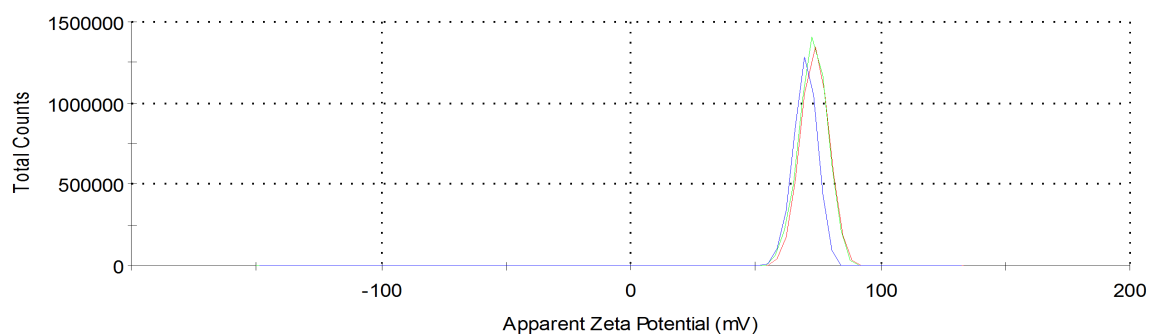
(b)



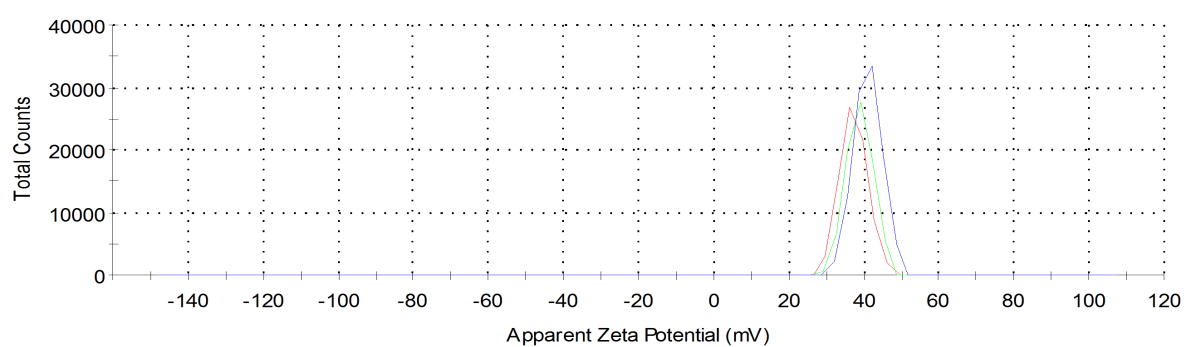
(c)

Figure E.1: Zeta potential for: a) Amber 2009; b) Amber 2012; c) Amber 2013.

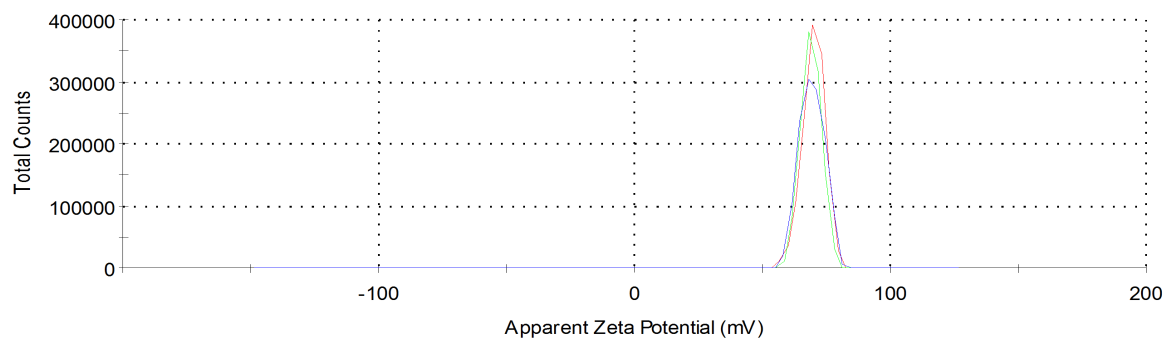
APPENDIX E. ZETA POTENTIAL OF THE SURFACTANTS



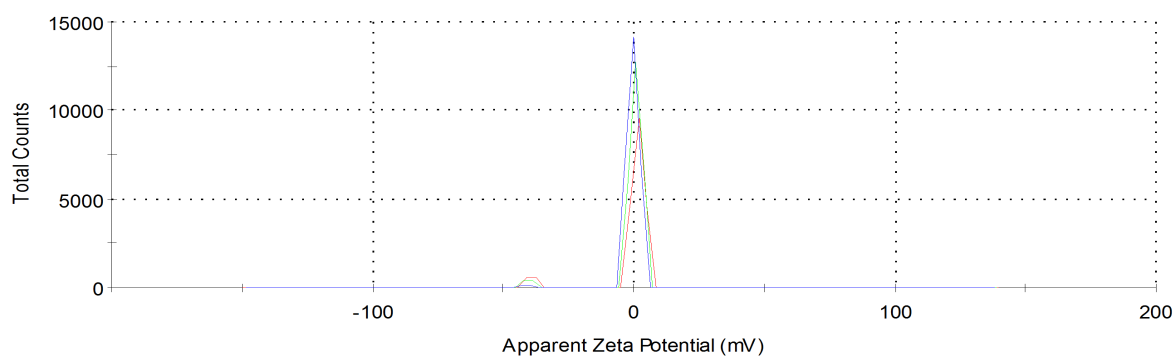
(a)



(b)



(c)

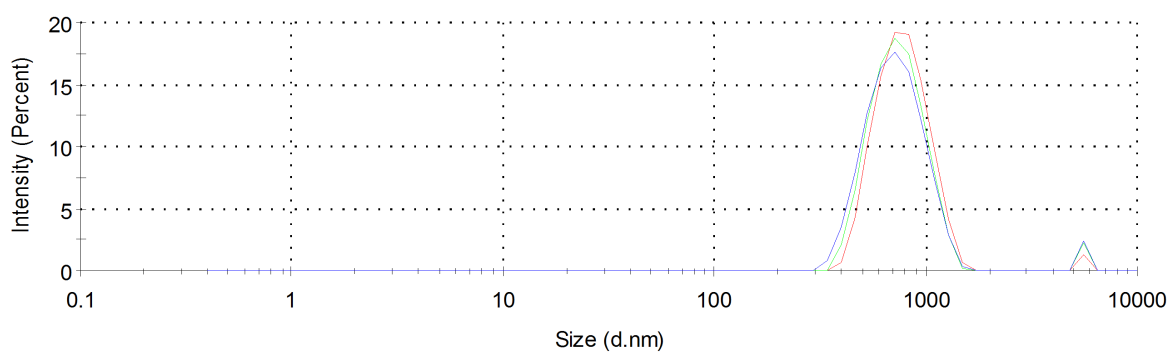


(d)

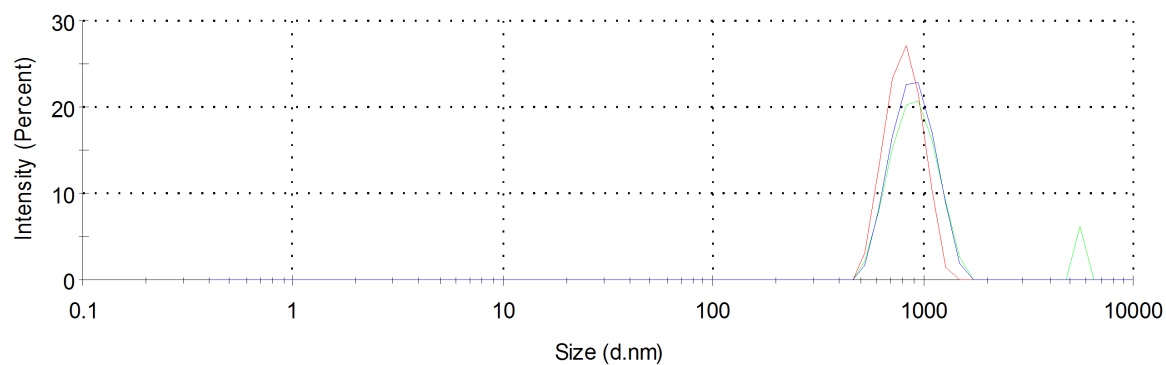
Figure E.2: Zeta potential for: a) Amber 2014; b) poliDADMAC HMW; c) poliDADMAC MMW d) Pluronic F-127.

Appendix F

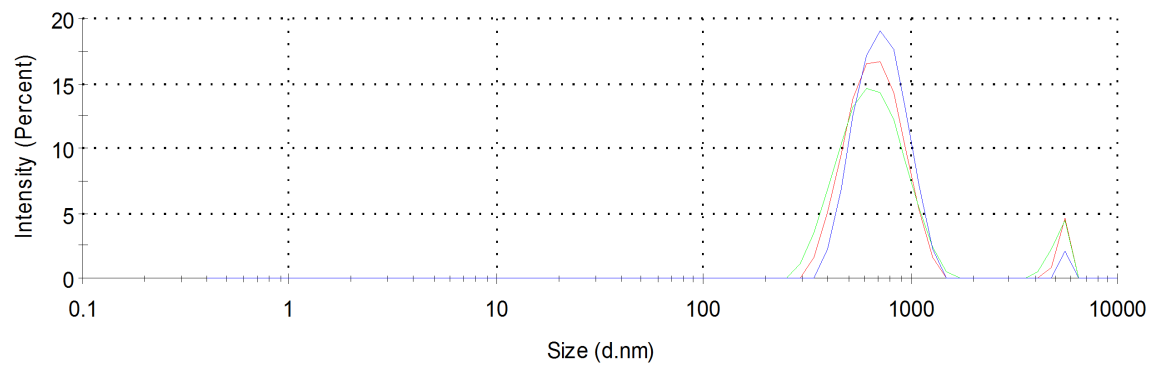
Size distribution by intensity of the MWCNTs dispersions with surfactants



(a)



(b)



(c)

Figure F.1: Size distribution by intensity of MWCNTs dispersions using: a) 1% Amber 2009; b) 1% Amber 2013; c) 1% Amber 2014.

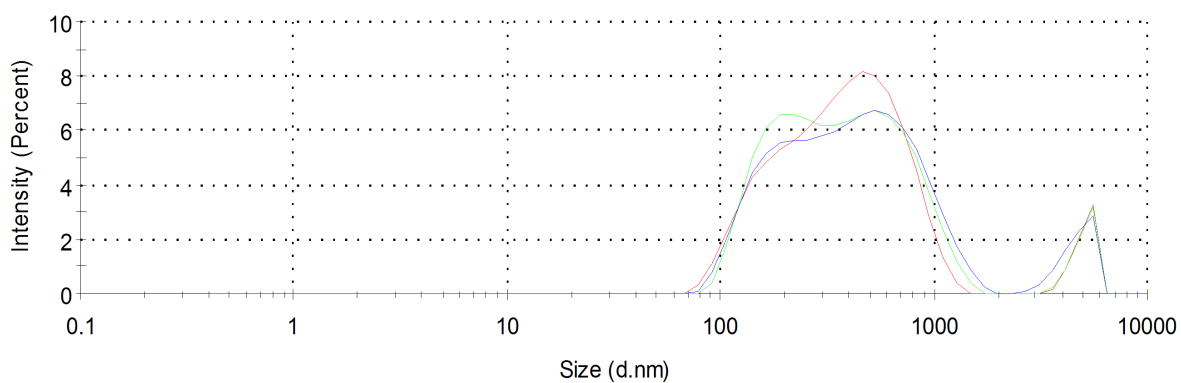
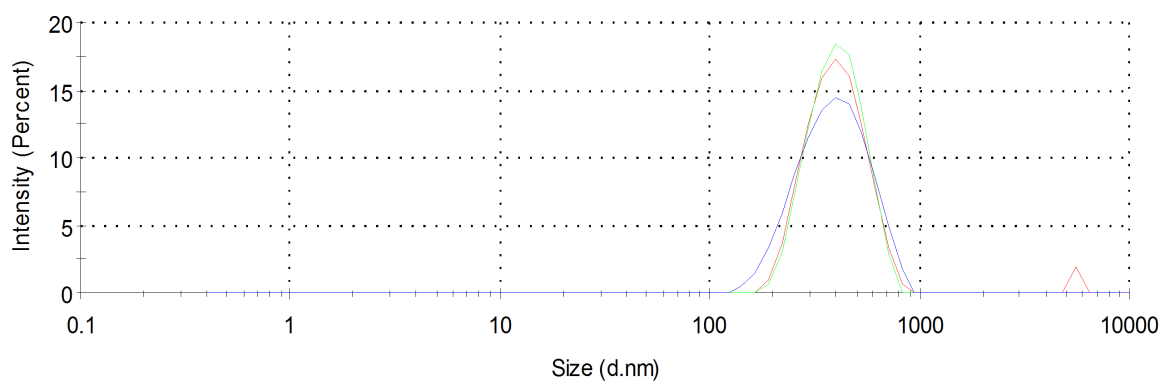
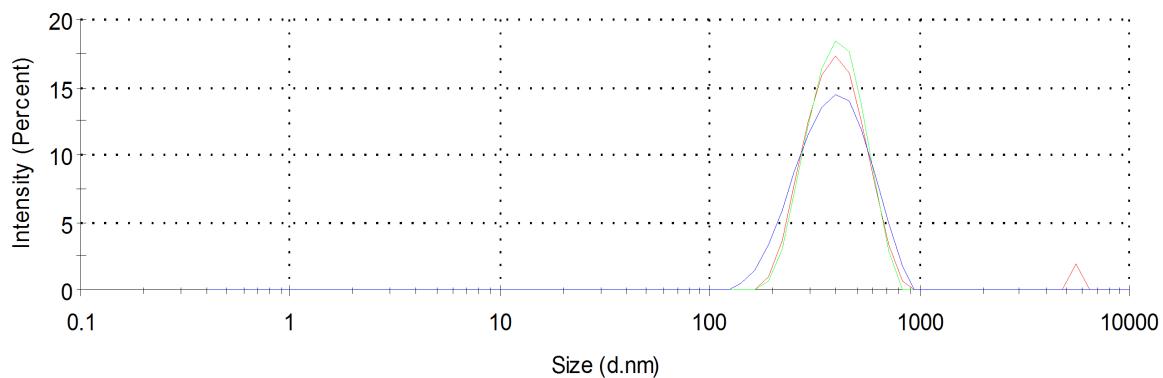
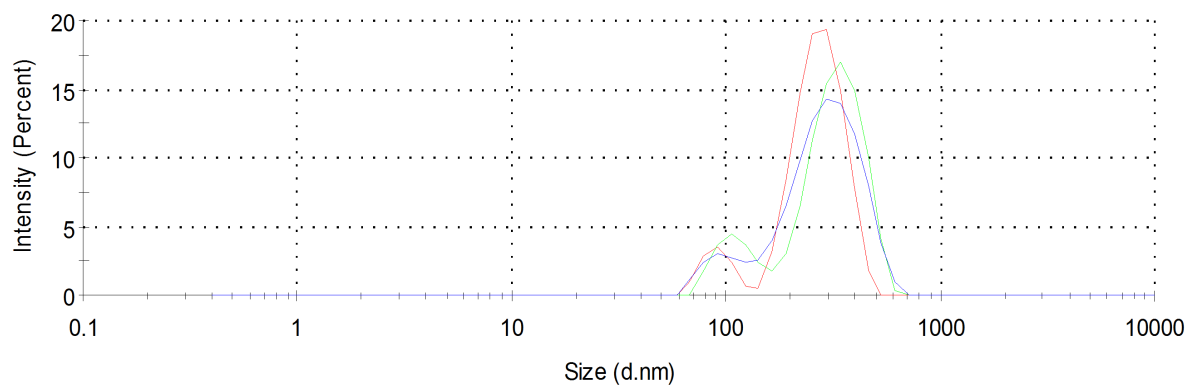
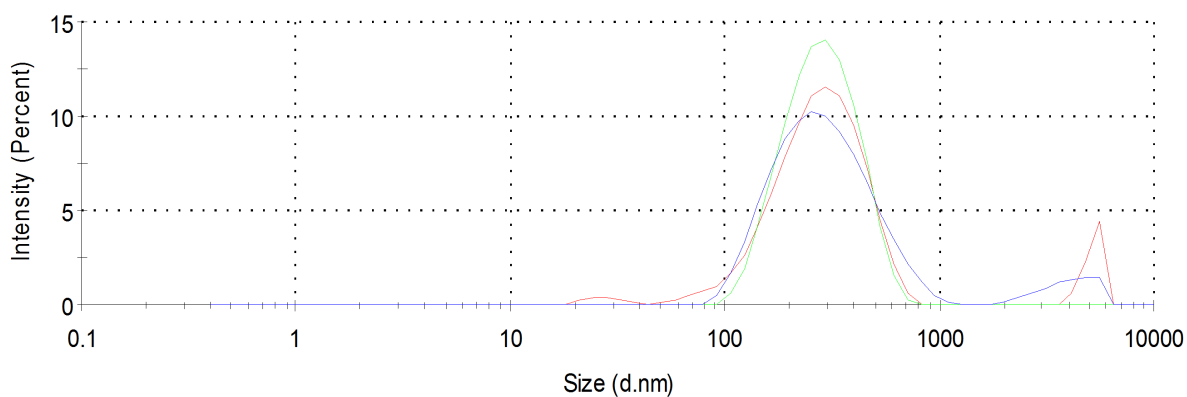


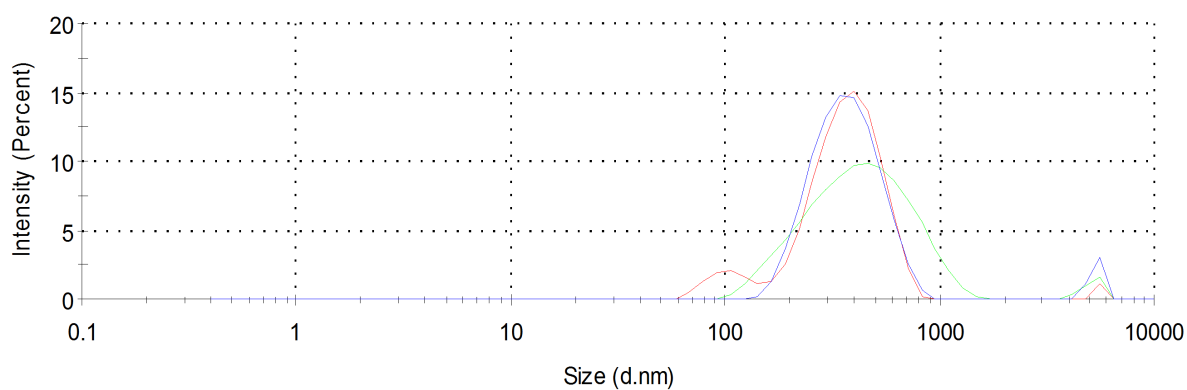
Figure F.2: Size distribution by intensity of MWCNTs dispersions using: a) 1% polyDADMAC HMW; b) 1% polyDADMAC MMW; c) 1% Pluronic F-127.



(a)

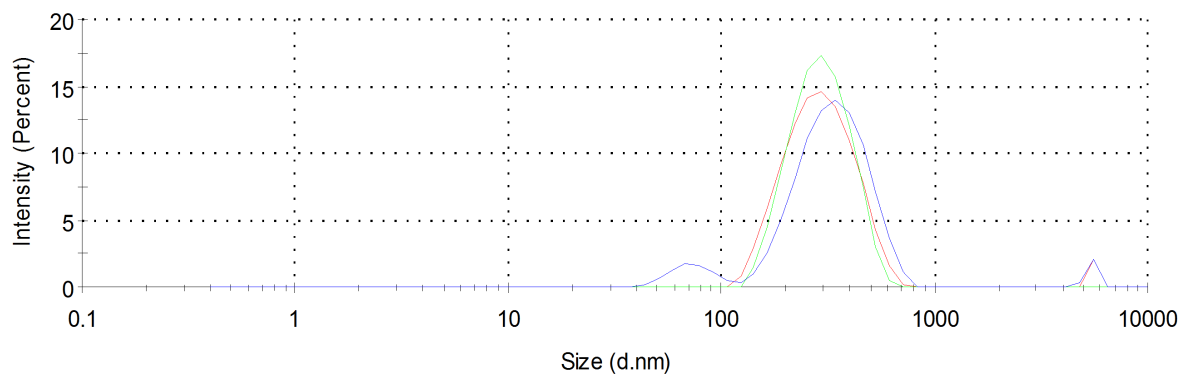


(b)

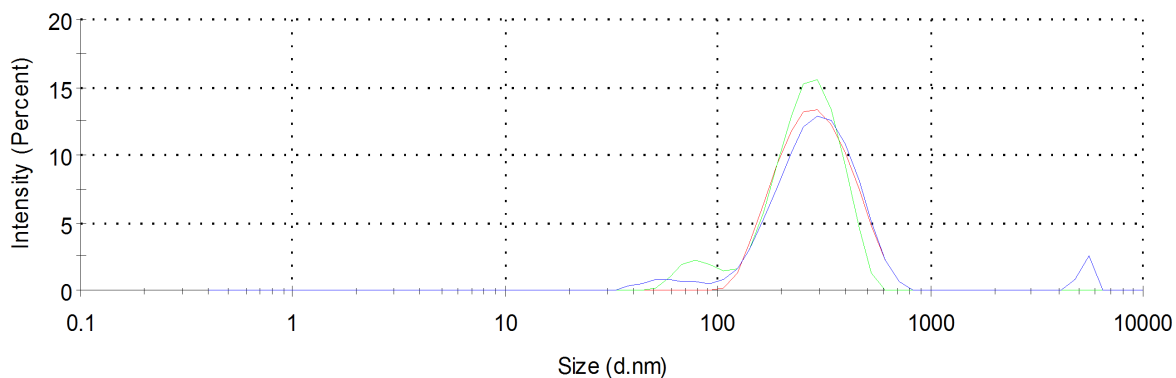


(c)

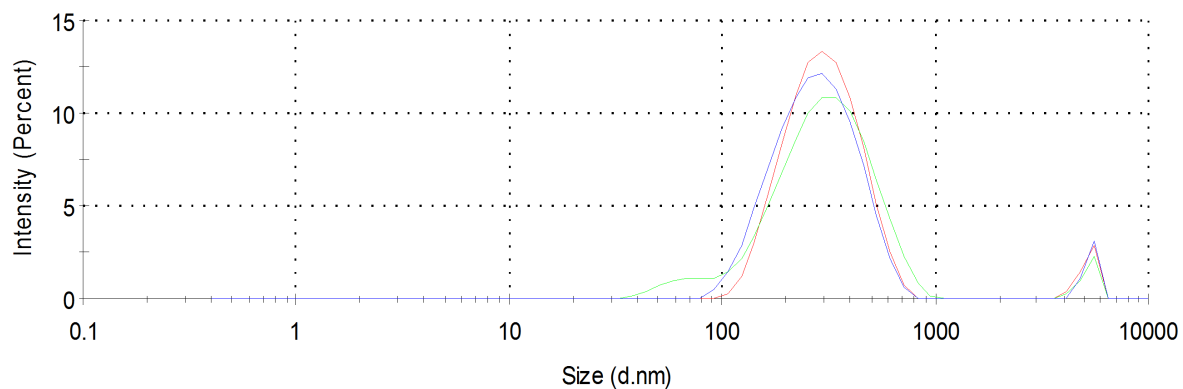
Figure F.3: Size distribution by intensity of MWCNTs dispersions using: a) 0.1% Amber 2009; b) 0.1% Amber 2012; c) 0.1% Amber 2013.



(a)

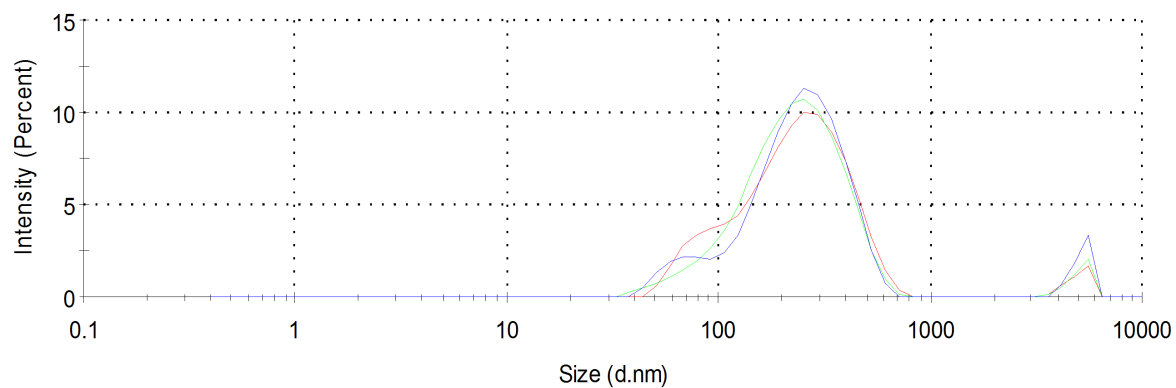


(b)

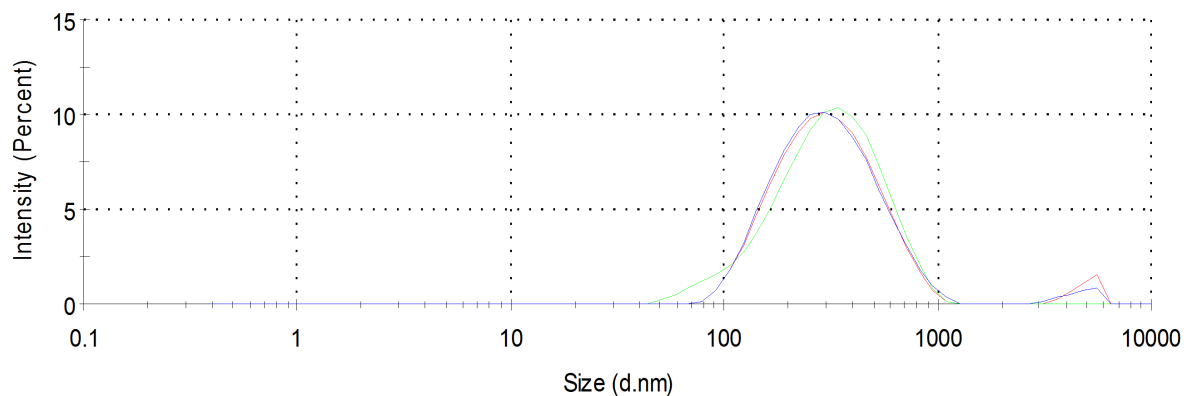


(c)

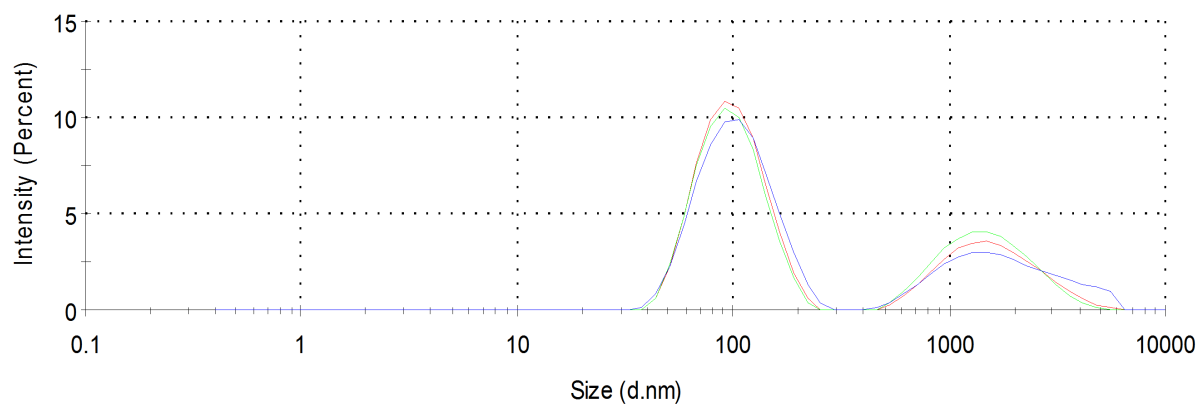
Figure F.4: Size distribution by intensity of MWCNTs dispersions using: a) 0.1% Amber 2014; b) 0.1% polyDADMAC HMW; c) 0.1% polyDADMAC MMW.



(a)



(b)



(c)

Figure F.5: Size distribution by intensity of MWCNTs dispersions using: a) 0.1% Pluronic F-127; b) 0.1% Pluronic F-127 + polyDADMAC MMW; c) 0.1% Glycerox + polyDADMAC MMW.