NANOTECHNOLOGY IN CONSTRUCTION: TOWARDS STRUCTURAL APPLICATIONS

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Dissertation to obtain the Master of Science Degree in

Civil Engineering

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ABSTRACT

Nanotechnology is a revolutionary vector of technology development. It concerns the management of matter at the nanometer-scale (one billion times smaller than a meter). Its potentialities have changed the perspectives, expectations and abilities to manipulate the material world. Several technological areas have been largely affected, from chemistry to physics or electronics to mechanics. The construction industry has been given increasing attention to the investigation and use of nanomaterials, which justified this work. It is the expectation of the research community that a new generation of structures with enhanced mechanical and durability properties can be achieved with the use of nanomaterials.

The main applications of nanotechnology reported in this paper covers concrete, polymeric and ceramic materials. This work focuses the structural applications of nanomaterials within these areas of the construction sector, identifying the main developments, potentialities and advantages of the use of nanomaterials. However, the manipulation of materials at such a small scale raises many challenges and misunderstood aspects that are also going to be addressed.

Considering all the aspects combined, some future routes and developments with potential to be addressed by Portuguese scientific research institutions are finally proposed.

Keywords: Nanotechnology; concrete; polymer nanocomposites; ceramic nanocomposites; nanomaterials.

RESUMO

A nanotecnologia representa um importante vector do desenvolvimento tecnológico. Resumidamente, a nanotecnologia representa a manipulação da matéria à escala nanométrica (10^9 vezes mais pequena do que o metro). As suas potencialidades têm alterado as perspectivas, expectativas e possibilidades na manipulação do mundo material. Ao longo dos anos, várias áreas têm sido vastamente afectadas pela introdução da nanotecnologia, desde a Química à Física ou da Electrónica à Mecânica. A indústria da construção tem aumentado a sua atenção no que respeita à investigação e uso de nanomateriais. Este crescimento na investigação e uso de nanomateriais, juntamente com as elevadas expectativas da comunidade científica na criação de uma nova geração de materiais com propriedades mecânicas e de durabilidade aumentadas, justificou este trabalho.

As principais aplicações da nanotecnologia desenvolvidas neste trabalho envolvem a produção de betão reforçado com nanopartículas e o desenvolvimento de materiais compósitos poliméricos e cerâmicos, com principal enfoque nas aplicações estruturais deste tipo de materiais. O objectivo passa pela apresentação dos principais desenvolvimentos, potencialidades e vantagens no uso dos nanomateriais nestes três âmbitos. Contudo, a manipulação de materiais a uma escala tão pequena resultou em novos desafios e questões por resolver que se pretende também aqui identificar.

Considerando estes diferentes aspectos nos temas propostos, pretende-se finalmente apresentar possíveis perspectivas para desenvolvimentos futuros que possam ser levados em consideração pelas instituições Portuguesas de investigação científica.

Palavras-Chave: Nanotecnologia; betão e cimento; nanocompósitos poliméricos; nanocompósitos cerâmicos; nanomateriais.

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ACRONYMS INDEX

CFRP - Carbon Fibre Reinforced Polymers

CHHC - Carbon Hedge Hog Cement

CH - Calcium Hydroxide

CMCs - Ceramic Matrix Composites

CNTs - Carbon NanoTubes

C-S-H - Calcium Silicate Hydrate

FESEM - Field Emission Scanning Electron Microscopy

FRP - Fibre Reinforced Polymers

GO - Graphene Oxide

HPSCC - High-Performance Self-Compacting Concrete

ITZ - Interfacial Transition Zone

nAl - Alumina

NCa - Calcium Carbonate nanoparticles

NCl – NanoClay

NCr - Cr_2O_3 nanoparticles

NF - Fe_2O_3 nanoparticles

NMs - Nanomaterials

NOx - Nitrogen Oxides

NPs - Nanoparticles

NS – Silica nanoparticles

NT - TiO_2 nanoparticles

MMCs - Metal Matrix Composites

MMT - Montmorillonite

MWCNTs - Multi-Walled Carbon NanoTubes

OPC - Ordinary Portland Cement

PC - Polymer Concrete Composite

PMCs - Polymer Matrix-based Composites

SBR - Styrene Butadiene Rubber

SCI - Science Citation Index

SEM - Scanning Electron Microscope

SF - Silica Fume

SHM - Structural Health Monitoring

SiC - Silicon Carbide

SWCNTs - Single-Walled Carbon NanoTubes

UHPC - Ultra-High Performance Concrete

ZTA - Zirconia Toughened Alumina

1. INTRODUCTION

1.1 Preliminary considerations

The speech of physician Richard Feynmam, entitled “There’s plenty of room at the bottom” and held in 1959 in a Meeting of the American Physics Society, is considered the beginning of the nanotechnology era (Feynmam, 1959).However, the term “Nanotechnology” was only presented for the first time in 1974, by Professor Norio Taniguchi, meaning the processing of materials, atom by atom or molecule by molecule (Taniguchi, 1974).

Nowadays, nanotechnology is a major vector of technological development. Its impact on Society has been compared to electric power at the beginning of the XIX century. Nanotechnologies have changed the perspectives, expectations and abilities to manipulate the material world. The possibility of manipulating structures at nanoscale has enabled the emergence of new materials with novel functionalities and improved characteristics. Several sets of technological areas and industrial activities were affected, from chemistry to physics, medicine to biology, electronics to mechanics, and sports to food industry.

In addition to these areas, the construction industry must also be considered since the application of nanotechnology to some components and processes of construction is now increasing. Although construction industry is still considered a conservative and traditional area of industrial activity, the possibilities and perspectives that nanotechnology provides have led to a paradigm shift. Additionally, both economic and environmental considerations have been forcing this sector to adopt new technologies, manufacturing processes and materials.

In this sense, nanotechnology came up as a great opportunity, due to the original physical, chemical and thermal characteristics of nanomaterials (NMs) primarily caused by the nano-quantum dimensional surface effects. Currently, there are several different applications in the construction industry. The report RILEM TC 197-NCM, “Application of Nanotechnology in construction” was the first document to summarize the potential of nanotechnology in the development and enhancement of construction and building materials (Zhu et al, 2004). Since then, many authors have subjected the same issue. For example, Lee et al. (2010) noted that NMs will likely have a greater impact on the construction industry than on any other sector of the economy. Currently, biomedical and electronics applications take great advantage on the use of NMs, but various authors cited many potential applications in the construction industry (Hanus and Harris, 2013):

- Improve the primary properties of traditional construction materials (e.g. concrete). For example, noteworthy improvements in concrete strength, durability and sustainability are being achieved by using various nanoparticles (NPs);
- Add new functionalities to existing materials, such as self-cleaning, antimicrobial and pollution reducing properties to paints, coatings or glass. In this field, environment-responsive anticorrosion coatings formed using nano encapsulation techniques are showing promise in laboratory settings;
- Create new materials, such as silica aerogels that fill an existing need for a thinner, translucent and yet effective insulation, or nanoencapsulated corrosion inhibitors to fight steel corrosion;
- Produce self-sensing structures, which means the opportunity of bridges and buildings to sense their own cracks, corrosion and stresses, which may eventually cause structural failures.

In this sense, several applications have been developed for this sector in the last years, improving the performance and durability of materials, as well as the energy efficiency and safety in buildings. The variety of applications ranges from more durable concrete to self-cleaning windows and walls.

However, there are critical barriers to be overcome to increase the market penetration of these new products and technologies. The Final Report of “ObservatoryNano” (2009) presented two important barriers: (i) the cost of new processing technologies and new materials as the biggest barrier and (ii) the consumer skepticism to the introduction of such high-performance materials.

Unfortunately, awareness of nanotechnology and NMs applications in construction among the biggest stakeholders is remarkably low and there are still some difficulties to distinguish between what is available now and what is theoretically possible and may exist in the future (Hanus and Harris, 2013). Based on a series of surveys done to the personnel involved in the construction industry, the RILEM report suggested that nanotechnology was perceived as expensive and too complex to explain to clients who want a structure built as soon and as economically as possible (Zhu et al, 2004).

Finally, there are still some reasonable concerns about potential adverse health and environmental effects in the use of NMs because the wide range of properties that make NMs so useful in increasing properties can also cause potential problems if the material is not properly used (Lee et al, 2010). Table 1.1summarizes the main benefits and barriers of the use of nanotechnology in the construction industry. All of these aspects will be discussed in this dissertation, presenting the benefits and drawbacks in using different NMs in the most used materials in the construction industry.

1.2 Objectives

The new paradigm observed in the construction industry is characterized by the openness to the introduction of new technologies in methods/processes and by new perspectives concerning the use of nanotechnology in the “next generation” of materials. In fact, the number of publications and results observed in the last couple of years on this topic has increased enormously. In that sense, the reorganization of the current level of knowledge is perfectly justified. This is, indeed, the main purpose of this dissertation: to summarize the recent and to point out some future developments on the application of nanomaterials in construction. Within this revision, this thesis will focus in particular those with impact on the structural behaviour in order to understand how nanotechnology can play an important role in a near future. In fact, the key to the implementation of nanotechnology in the market is to understand the specific advantages, risks and implications of NMs and products before they are widely used.

Taking into account the impossibility of discussing all the areas of the construction industry where nanotechnology has been applied, it was decided to address the following sub-areas more related with structural applications:

- Cementitious materials - cement and concrete;
- Polymers nanocomposites;
- Ceramics nanocomposites.

The study developed on each topic required a detailed process of search and information treatment in order to organize the present knowledge in the research community. Therefore, the main objectives of this dissertation are:

- In-depth search in the various scientific databases for articles related with the topics presented above;
- Organization and selection of the articles according to the sub-theme proposed. Selection of the most relevant topics for which the summary of knowledge is justified;
- Summary of the main developments in each topic;
- Critical analysis of recent developments, in order to suggest/predict future developments on each area;
- Summary and identification of the main problems found in the development of nanomaterials in construction and identification of the key factors that are barriers to a more disseminated introduction in this industry.

Table 1.1 - Main benefits and barriers of the use of nanotechnology in construction industry

BENEFITS	Materials and properties	- Strength and durability (e.g. cementitious composites) - Wear and tear resistance - Corrosion resistance (e.g. coatings) - Fire resistance and retardants - Aesthetics - Heat insulation (e.g. glass) - Self-cleaning (e.g. concrete, glass) - Bactericidal capacity (e.g. coatings) - Photocatalytic activity - Promotes air pollution reduction (e.g. cements and coatings)
	Economic	- Improves life-cycle and maintenance costs - Pricing and profit - Customer satisfaction - Market value and brand image
	Sustainability	- Energy efficiency - Reduces material consumption - Social and ethical benefits - Reduced levels of several environmental pollutants (e.g. CO2 associated with cement production) - "Green nano-construction"
BARRIERS	Costs and manufacturing	- Costs of materials and equipment - Costs of commercialization - High initial investment by nanotechnology companies - Lack of properly trained personnel and costs of training
	Environmental	- Safety and security concerns - Potential toxicity to the workers
	Social	- Regulatory and legal issues - Scepticism of the main industry stakeholders and consumers

1.3 Global knowledge and market distribution

The nanotechnology revolution experienced in the last few years had a huge impact on various science fields (chemistry, engineering, biology), also affecting the construction industry. Conceptually, nanotechnology may be defined as the ability to create new structures at the smallest scale, using tools and techniques that allow the understanding and manipulation of matter at nanoscale, generally from 0.1 to 100 nm (Zhu et al., 2004). Although this is the most often used definition, a size limitation of nanotechnology to a range below 100 nm seems to exclude numerous materials and devices, particularly in the pharmaceutical area. For that reason, some experts disagree with a rigid definition based on a sub-100 nm size. To circumvent this divergence, Bawa et al. (2005) proposed a definition unconstrained by any arbitrary size limitations: "…*The design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property*…".

Nanotechnology covers nanomaterials, such as nanoparticles (NPs), nanotubes, nanostructured materials and nanocomposites, nanotools (tools and scanning probe microscopes) and nanodevices (nanosensors and nanoeletronics). The reports of Bcc Research (Nanotechnology – A realistic market assessment) allow perceiving the outstanding extent and impact that nanotechnology currently has in various markets. Figure 1.1 shows the evolution of global nanotechnology market between 2009 and 2015. It shows a remarkable increase of approximately 122% between 2009 and 2015, mainly explained by commercialization of nanomaterials, such as nanotubes and NPs. The increase of research projects in recent years partially explains this high demand and commercialization of nanomaterials. Moreover, Bcc Research predicts 64.2 billion dollars by 2019, which represents an increase of 19.8% per year.

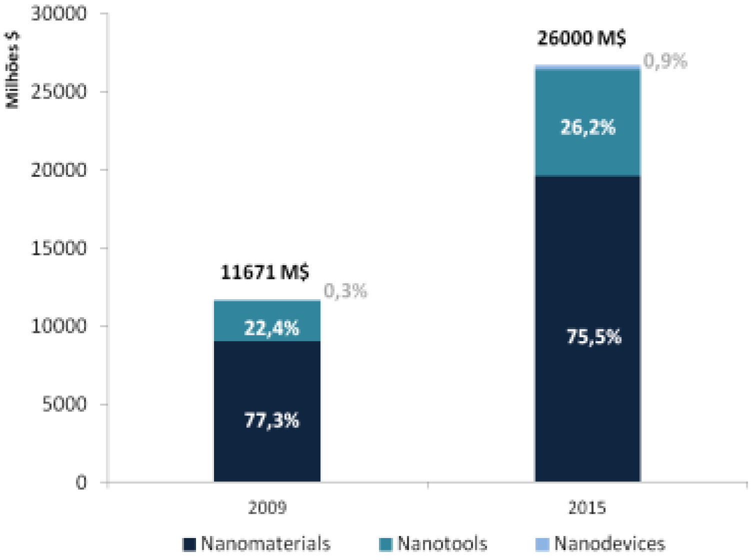

Figure 1.1 - Global nanotechnology market evolution between 2009 and 2015 (values obtained from Report NANO31D - Bcc Research).

These values are explained because nanostructures and nano-modifications may lead to completely distinct composite materials, both at a macroscopic scale and in their properties and performance. The range of application of nanotechnology is, for this reason, very large. Figure 1.2 shows the impact that nanotechnology has in various technical areas. Within them, electronics, biomedical and materials (textiles) take advantage of the development and impact of nanotechnology methods. Based on Figure 1.2 it seems that the construction industry is dissociated from nanotechnology. In fact, due to the tendency of the construction industry to be fragmented, rationally more conservative and associated with less funded research, the implementation of nanotechnology in this industry is slower than in others industries. Additionally, the construction industry stakeholders often perceive nanotechnology as expensive and too complex to explain. The need to build a structure "as soon and economical as possible" precludes all the nanotechnology advantages. However, as many authors stated (Lee et al. (2010), Zhu et al. (2004)), NMs will have in the short term a greater impact in construction industry than any other industry area.

In fact, the potential to apply NMs in construction is high and involves almost all technical areas within this industry. Figure 1.3 summarizes the impact of nanotechnology within the different areas of construction. Composites (polymeric, ceramic and metallic) and coatings take great advantage from the application of nanotechnology. Also concrete plays an important role, with the potential to develop new products, more durable and with lesser reduced pollution effects. From 2007 until now it is also relevant to register an increasing interest of the research community on the application of NMs in steel that currently certainly constitutes more than 5% of the overall construction industry.

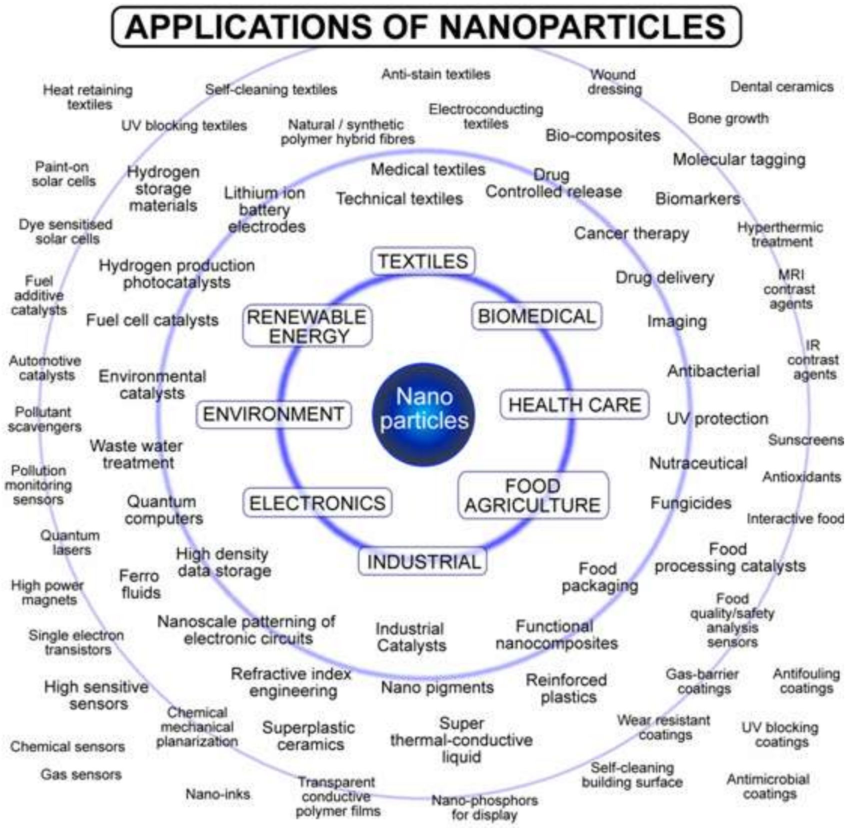

Figure 1.2 - Applications of NPs in different industrial areas (Tsuzuk, 2009).

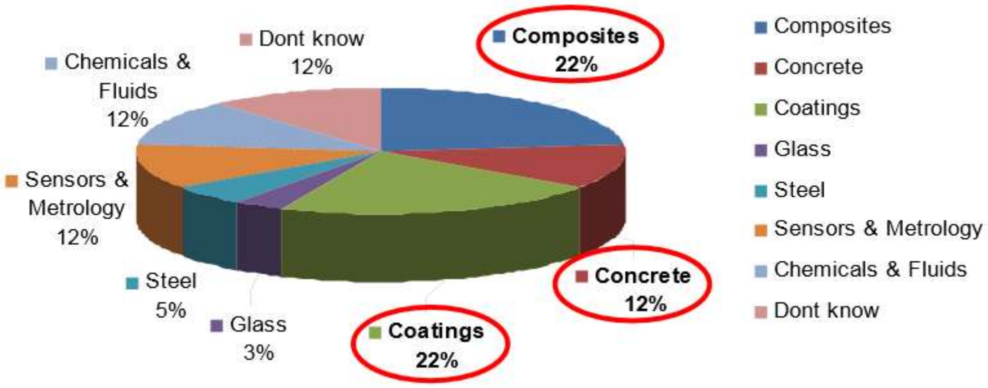

Figure 1.3 - Major impacts of applications of nanotechnology in construction materials (Tsuzuk, 2009).

1.4 Materials

Considering the aspects mentioned before, the following sections summarize the evolution of the market and scientific research on the issues accessed in this dissertation, namely focused on materials for structural applications: (i) cement and concrete, (ii) polymers, and (iii) ceramics.

1.4.1 Cement and concrete

Concrete is the leading material in structural applications, where stiffness, strength and cost play a key role in its high attributes. Typical concrete consist of Ordinary Portland Cement (OPC), inert materials such as sand, coarse aggregates and additions, admixtures and water. It is this combination that allows concrete to be produced in a fluid form that can be pumped and moulded, justifying its great application in construction industry. According to the Activity Report of European Cement Association (CEMBUREAU) the total production worldwide of cement in 2013 was approximately 4 billion tonnes, the highest number over the last years and this trend does not seems to stop. Figure 1.4 allows making some comments on the evolution of cement production by region from 2001-2013. It can be seen that, even with the breakdown of investment in construction industry market (1284.6 billion Euros in Europe) (CEMBUREAU, 2013) and the emergence of new materials with improved characteristics (such as steel), the production of cement in Europe, Oceania and America stayed approximately stable. Contrary, a remarkable increase in cement production is visible for the regions in expansion (Africa and Asia) thanks to their high needs of buildings and infrastructures. Among them, China is currently responsible for 58.3% of world cement total production, according to CEMBUREAU.

These facts support the idea that cement and concrete will continue to be the most used material in construction industry. However, some important issues came up regarding their massive use and production. Mehta and Monteiro (2010) presented two major challenges that the production of concrete has to face in the following years. To begin with, one should consider the environmental impact that the production of concrete has in terms of natural resources and pollutants emissions. According to the authors, and reporting to present values, the world's demand/year of cement, water and aggregate represents 4, 2.7 and 24 billion tonnes, respectively. In terms of pollutants emissions, Naik (2008) reported that the production of one tonne of OPC produces about one tonne of CO_2 and other greenhouse gases. This means that the production of OPC only by itself represents 4 billion tonnes of CO_2 and other greenhouse gases emissions (approximately 10% of total CO_2 emissions according to CO_2Now Association). Additionally, the necessity of 24 billion tonnes/year of aggregate results in the depletion of natural resources. For example, as the supply of good-quality limestone to produce cement decreases, producing adequate amounts of OPC for construction will become more difficult. The second challenge is related with the long-term durability and civil infrastructure deterioration. Concrete durability is highly affected by exposure conditions and the environment. Sulphate attacks, alkali silica reaction and corrosion of reinforced concrete are important issues to take into account when concrete's performance is evaluated. In addition, there are still some issues of fundamental science to be resolved related with the complex chemistry and physical structure of cement hydrates.

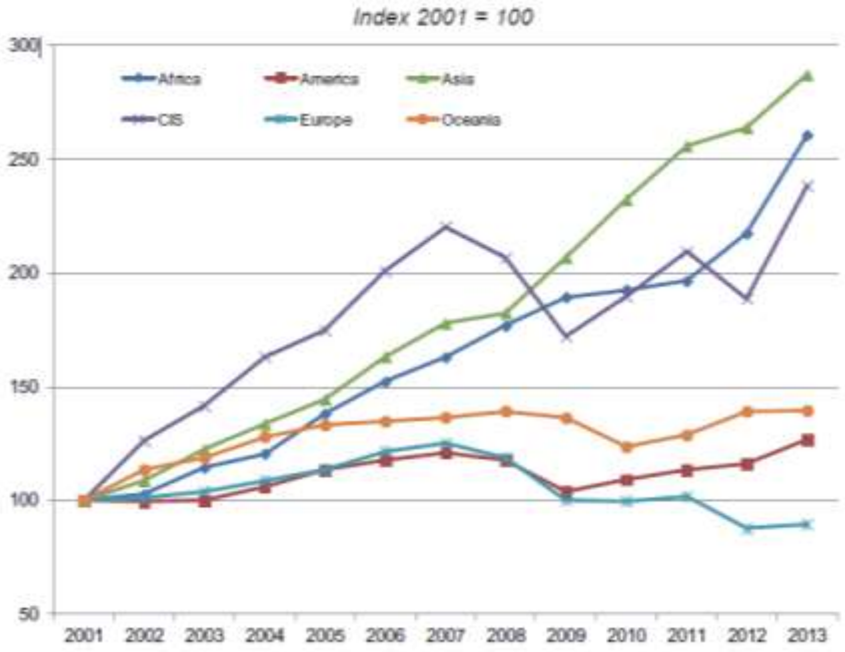

Figure 1.4 - World cement production by region evolution 2001-2013 (CEMBUREAU, 2013).

To overcome these aspects, the trend in the construction industry has been to reduce the use of OPC in concrete production by replacement with other materials, named blended cements. For example, the use of wood fly ash, slag, silica fumes or finely ground cullet replacing cement in concrete production has led to reduced greenhouse gases emissions, reduced fuel consumption in the final cement production and recycling of some of these materials (Naik, 2008). However, with the emergence of nanotechnology and NMs a wide range of new opportunities have opened. Figure 1.5 allows drawing some comments on the research evolution in the field of nanotechnology in concrete. It shows the evolution of the number of publication indexed in SCI Web of Knowledge per year, since 2000, and corresponding to keywords "concrete and nano" in searched "Topic". It is easily seen that the works on concrete nanotechnology rapidly increased from 1 in 2000 to 133 in 2013. The number of published works steadily increased from 2000 to 2009, but from 2009 to 2011 it displayed a huge rise mainly due to the advent of NMs "from lab to society", through information media. From 2011 till 2013, the number of published works is nearly the same. However, the number of current research teams working on the concrete nanotechnology is still high.

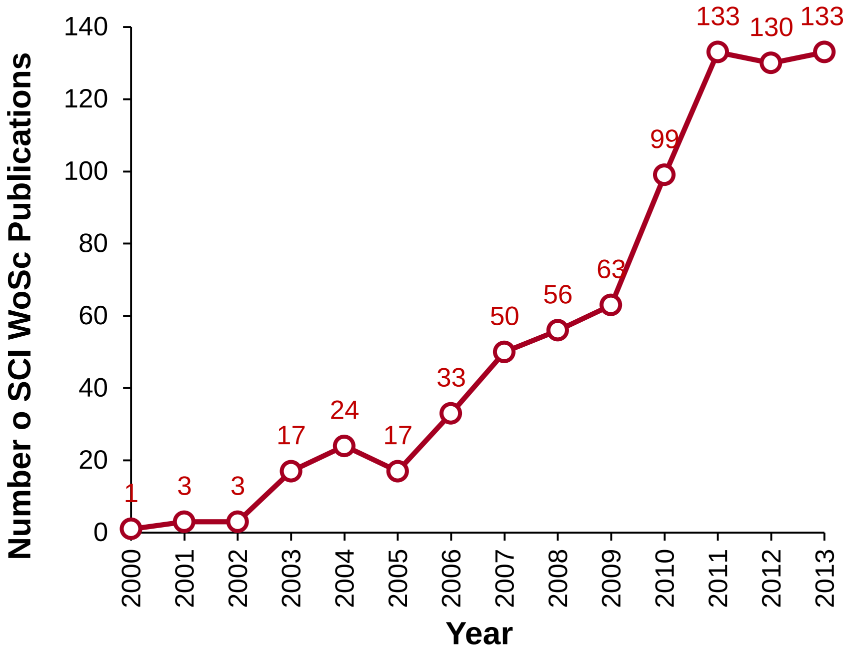

Figure 1.5 - Number of publications per year indexed in SCI Web of Science matching keywords “concrete and nano” in searched “Topic”.

Figure 1.6 shows the yearly patent publication trend for nanotechnology applications in the cement industry. As shown in Figure 1.5, there is a high rate of growth in the number of patents published until 2011, with a maximum of 111 patents published in this year, which support the idea that there is a high output of commercialization and research in this field.

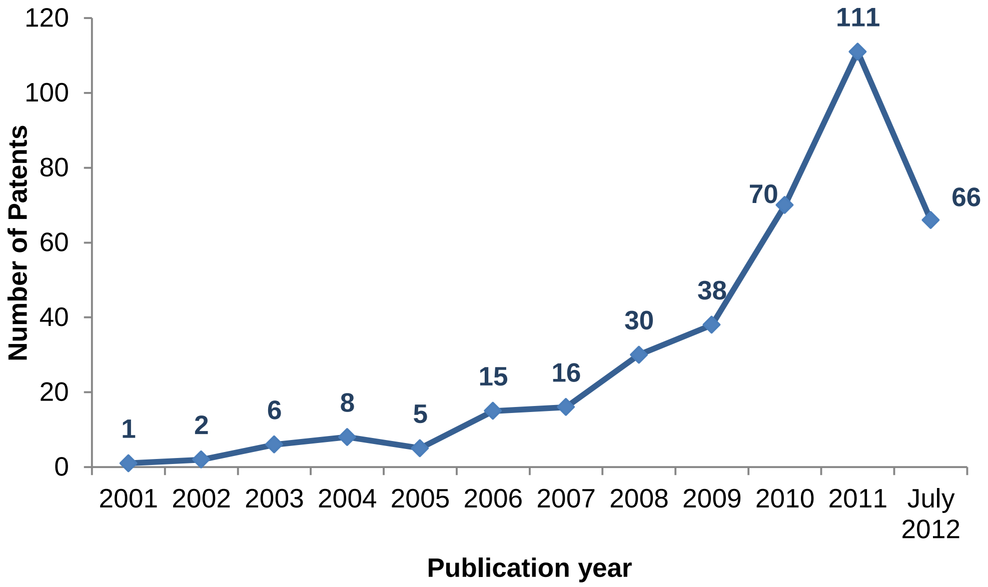

Figure 1.6 - Yearly patent publication trend for nanotechnology applications in the cement industry (adapted from Nanowerk, 2012).

The high level of attention that nanotechnology has captured in the last years is not only justified by the impressive impact of its use, but mainly by highly improved properties of NMs when compared to those manipulated at macroscale. For example, the improvements of the addition of NMs to the cement and concrete production include better cement hydration, higher compressive strength, higher ductility and energy dissipation. However the high complexity associated to structures' manipulation at nanoscale makes this a field going through intense development and research. Chapter 2 approaches this subject by reviewing the state-of-art on the use of NPs in concrete's and cement's based materials.

1.4.2 Polymers

Polymers have become increasingly important in the construction industry in the past decades with expanding applications. Initially, unreinforced polymer composite materials were used by the construction industry in non-load bearing applications. The introduction of reinforced polymer composites extended the range of application of these types of materials. Today, the construction sector is one of the world's largest consumers of polymer composites. Polymer composites bring a large range of benefits to the architecture and construction industry. To begin with, composites materials can significantly reduce the buildings' dead load, which allows a weaker foundation, a more manageable seismic design and smaller construction crane requirements. This results in material and cost savings. In addition, durability and weather resistance mean less maintenance and life-cycle costs. The relevance of polymers composites is so high that in 2009, the International Code Council voted to allow the use of composite materials for both interior and exterior wall applications, reflected in the code's last edition, where a section with fibre-reinforced polymer was included (Composites World, 2014). Within the European markets, Lucintel predicts a total market size of 2 billion dollars by 2016 for composites in construction, and a growth of 5.4% annually through 2014 in U.S. cast polymer market, which is the highest consumer of these types of materials. In fact, fibre reinforced polymers (FRP) are probably the most used polymer matrix-based materials within the construction industry. These materials were primarily developed for aerospace and defence industries but its use in civil infrastructure has gained great interest. The development made over the years enabled the use of FRP as structural elements in construction. FRP gains advantage over other construction materials thanks to their increased durability, high strength-to-weight ratio, ease and speed of installation, non-corrosiveness, low thermal conductivity and versatility. The effectiveness of FRP for strengthening and repair of structures is already well established (Humphreys, 2003). Over the years FRP are being used in bridge structures and their effectiveness for strengthening and repair purposes is already well established. Figure 1.7 and Figure 1.8 show two of the most common applications of FRP in construction, respectively the use of CRFP to reinforce columns and to replace a corroded concrete deck, with gains of easiness of construction and durability.

In addition to reinforcement of structures and replacement of existing structures, the use of FRP should also be seen as an opportunity to develop new types of materials, functions and designs. Figure 1.9 shows a remarkable example of a new design structure robotically fabricated in Stuttgart with glass and carbon composites, which would not be achievable with steel or concrete.

Apart from structural applications, polymer composites are also widely used in other areas of construction. Flooring, windows, cladding, membranes, insulation are some examples of other well established applications in construction. The emergence of nanotechnology and the opportunity of applying nanomaterials in composites production open new perspectives. Recently, polymer matrix-based nanocomposites (PMCs) have become a prominent area of research and development. The opportunity of applying PMCs in structural reinforcement and rehabilitation of damaged infrastructures, as well as working as new structural materials with increased load-carrying ability, justifies the increasing number of recent studies. In addition to mechanical properties, several other properties and potential applications are known such as barrier properties, flammability resistance, durability or improved electrical/electronic properties (Paul and Robeson, 2008). Figure 1.10 shows the evolution of the number of publication indexed in SCI Web of Knowledge per year, since 2000, corresponding to keywords “Polymer and nanocomposites” in the “Topic” field. It is possible to see that the works on PMCs increased tremendously from 204 in 2000 to 8034 in 2013. Moreover, it is clear that the number of published works steadily increased from 2000 to 2009, but from 2009 to 2010 there was a huge rise that may be explained (similarity to nanotechnology in cement and concrete) by the advent of nanomaterials through information media. After 2010, the growing trend was maintained and currently there is no expectation that it will slow down, which can sustain the success of further research projects.

Figure 1.7 - Test set-up of a CFRP reinforced column (Abdel-Hay, 2014).

Figure 1.8 - Replacement of a corroded concrete deck with a FRP deck, Indiana 2009. (ZellComp).

Figure 1.9 - Robotically fabricated pavilion in Stuttgart with carbon and glass FRP. (Evolo competition, 2013).

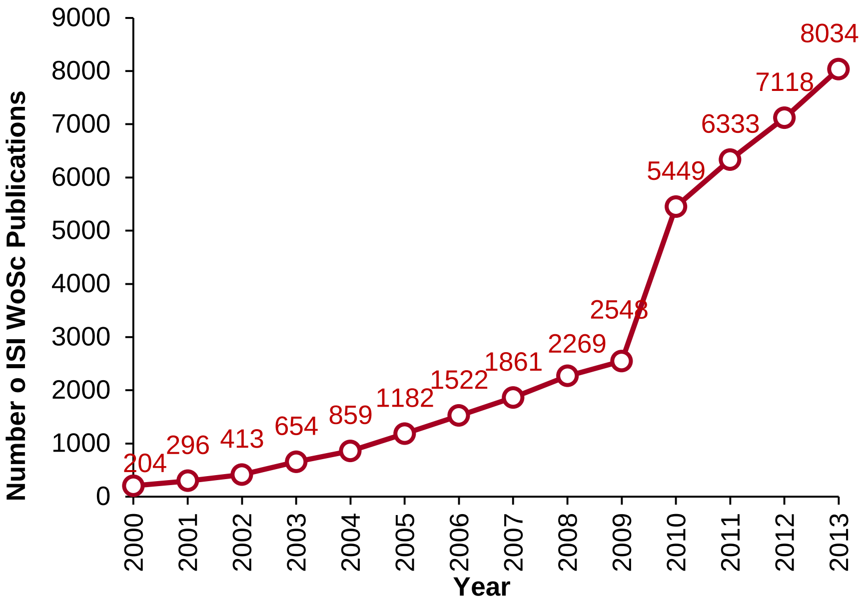

Figure 1.10 - Number of publications per year indexed in SCI Web of Science matching keywords “Polymer and nanocomposites” in the “Topic” field.

These facts support the idea that PMCs offer a great opportunity for development, namely in sustainable construction/green building application because of their efficiency and environmental protection.

1.4.3 Ceramics

Ceramic materials are extremely valuable for applications with demanding thermal and mechanical requirements. These materials are mainly made of two major types, monolithic and composites. Monolithic ceramics have attractive properties like high stiffness, strength and stability at high temperatures. However, monolithic ceramics tend to be brittle, mechanically unreliable and poor electrical conductors, which have limited their use and expansion for years. With the introduction of reinforcing phases made in different forms, including continuous or short fibres and particles, ceramic composites showed superior mechanical properties such as thermal shock resistance and toughness. Thanks to these improved properties, ceramic composites currently serve several industries including mechanical and chemical, aerospace and defence, and energy and environmental. Figure 1.11 shows the global market evolution of ceramic matrix composites between 2010 and 2015. It is possible to see a remarkable increase in all segments for the global market between 2010 and 2015. Mechanical/chemical and energy/environmental segments are the most relevant with an average increase of 7.7% per year. However, the main increase is in the segment “others” with an increase of approximately 13.1% per year, where the construction industry plays an important role to explain this increase.

In construction, ceramic products like floor, walls and roof tiles or bricks are important parts of a multi-billion dollar industry. The massive production of ceramic composite materials has opened the path to use ceramic construction materials with increased mechanical properties, particularly toughness resistance, thermal and chemical properties. Currently, the increasing interest by the research community in nanotechnology has also included ceramic matrix-based materials. Ceramic matrix nanocomposites (CMCs) can be extremely valuable for applications with demanding thermal and mechanical requirements. CMCs open the possibility of achieving damage tolerant quasi-ductile fracture behaviour, maintaining all the other advantages of monolithic ceramics at high temperatures. Additionally, CMCs may open new opportunities to use ceramic materials with different functions, eventually for structural purposes. All of these opportunities have been explored by the research community. Figure 1.12 shows a progressive increase in the number of publications per year since 2003. Despite this increase the number of publications within this issue is still significantly lower than those on nanotechnology in PMCs. Moreover, was observed a tremendous increase in PMCs between 2009 and 2010, which didn´t occur in CMCs. This could indicate that the potential and relevance perceived by research community for CMCs and its application is considerably smaller than those for PMCs.

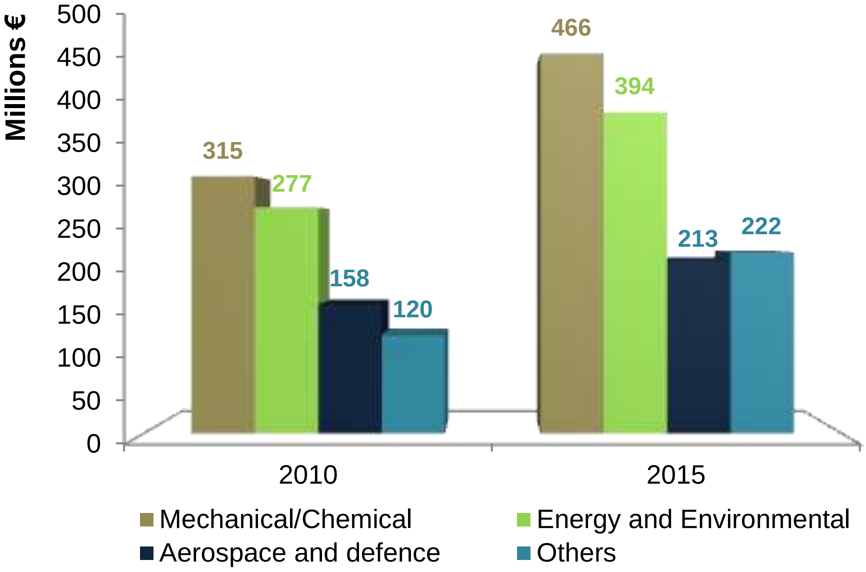

Figure 1.11 - Global market for ceramic matrix composites, 2010-2015 (adapted from Bcc Research, 2010).

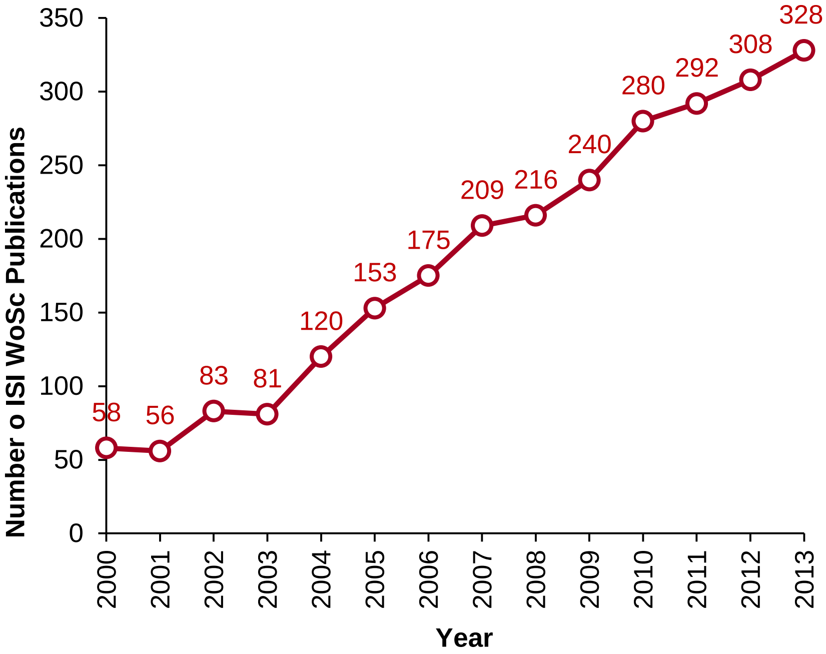

Figure 1.12 - Number of publications per year indexed in SCI Web of Science matching keywords “Ceramic and nanocomposites” in the “Topic” field.

Still, Chapter 4 presents this issue, reviewing the state of the art and presenting the main developments and the existence of opportunities for developing new high-performance materials with new functions in the construction industry.

1.5 Methodology

To reach the objectives described in section 1.2, the following work methodology was adopted:

- Initially, an extensive scientific search was undertaken with the purpose of making contact with the different scientific databases and also gathering a vast set of information on the topics treated in this dissertation. This research involved scientific databases such as ISI Web of Knowledge and Scopus. Master and doctoral dissertations, articles and reports presented in international conferences were also included in this search;
- All the information obtained was divided and structured according to the sub-theme (e.g. cementitious materials, ceramics); Thereafter, significant and substantial information was selected and summarized in order to develop the dissertation, regarding the structure proposed;
- An assessment of information on the various chapters was prepared. A critical analysis of the state-of-art of the different issues was made in order to suggest/present future developments to the scientific community (in conferences, seminars, and communications). Moreover, the effective introduction of nanomaterials in the construction industry was discussed. The main advantages and barriers to this implementation were analyzed.

Finally, it should be emphasized that review articles about each topic proposed were submitted for publication in international journals indexed in SCI (Science Citation Index).

1.6 Organization of the dissertation

Considering the objectives proposed, the dissertation was structured in five chapters. Besides the introduction (Chapter 1), the following three chapters develop each of the subjects mentioned above: cement and concrete, polymers and ceramics nanocomposites, respectively. Each chapter is structured according to the NPs used for the specific purpose. The final chapter presents an integrated view with the main conclusions of the work. The main contents of each chapter are succinctly presented next:

- **Chapter 2**: *Cement and concrete* - this chapter is focused on the potentialities of using nanomaterials as additives in concrete production. The opportunity not only of improving the physical and mechanical materials properties but also the environmental protection and energy saving have raised the interest of the research community on this issue. The review includes the addition of various NPs, such as nanosilica, nanoclay and carbon nanotubes, presenting a comparative analysis of the advantages and drawbacks of using each one. Some examples of effective applications of nanomodified cement-based materials are also presented.

- **Chapter 3**: *Polymers nanocomposites* - this chapter reviews the state-of-art on the use of NPs in polymer-matrix-based materials for application in the construction industry. The opportunity of using PMCs for sustainable construction/green building applications thanks to their efficiency and environmental protection is analysed. At the same time, the potential of using PMCs for structural reinforcement of existing buildings and developing new raw materials with improved mechanical properties is also assessed. The review includes a large range of NPs, namely graphene oxide, nano-titanium dioxide and nanosilica.

- **Chapter 4**: *Ceramic nanocomposites* - this chapter reviews the recent developments on the application of nanomaterials in ceramic matrix nanocomposites. It focus the nanomaterials with promising structural applications, such as silicon carbide and carbon nanotubes, describing how its superior thermo-mechanical properties, high thermal conductivity, hardness and low density can promote the development of new ceramic materials increasing the actual range of application in the construction industry.

- **Chapter 5**: *Integrated view* - Future developments, trends and conclusions - the final chapter presents a reflection on all the aspects developed in the previous chapters. The main conclusions are systematically presented, regarding the advantages of using nanomaterials in construction materials, with emphasis on structural applications. Also the main drawbacks and challenges that nanotechnology faces are discussed. Finally, the chapter includes some "hot topics" to be considered by the research community in future projects, particularly by Portuguese institutions, based on the conclusions of the whole work.

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2. CEMENT AND CONCRETE

The present chapter reviews the literature on the application of nanotechnology in the construction industry, with emphasis in concrete production. It is known that concrete is the leading material in structural applications, where stiffness, strength and cost play a key role in its high attributes. Concrete is a composite material at macroscale but its properties are highly influenced by meso and nanoscale structure. In this sense, nanotechnology has a high potential to contribute to the understanding of concrete´s behaviour, in order to improve its mechanical properties and reduce ecological and construction materials production costs (Raki et al., 2010).

Concrete´s nano-modification may be made in one or all of the phases: solid phase, liquid phase or in liquid-solid interfaces, which is possible because of its porous liquid-solid composition (Garboczi, 2009; Sanchez and Sobolev, 2010). However, controlling the process of nano-modification in these different phases represents a high complex subject making of this field an area of intense development and research. This high complexity is quite visible in the several cementitious and bituminous products that have been developed, where some important properties (such as compressive and tensile strength, ductility or shrinkage phenomena) were improved. Examples range (i) from UPHC (Ultra High Performance Concrete, e.g. Lehmann et al., 2009; Stengel, 2009) to CHHC (Carbon Hedge Hog Cement, e.g. Cwirzen et al., 2009), (ii) from autoclaved aerated concrete (Laukaitis et al., 2012) to self-compacted lightweight concrete (Madandoust et al., 2011) and, still, (iii) from calcium-leached cement-based materials (Bernard et al., 2003) to recycled aggregates concrete (Li et al., 2012).

These improvements have been achieved thanks to the nanomanipulation of hydration products of concrete, such as C-S-H NPs, which have enabled the production of hardening accelerators, such as Master X-seed, by BASF Construction Solutions (2014). These products offer different benefits such as early strength acceleration at low, ambient and heat curing temperatures, improved concrete durability and reduced water absorption.

On the other hand, improvements in concrete properties have resulted from the addition of new NPs in concrete mixes mainly by replacing cement. This chapter will mainly focus this second topic.

This perspective of development in concrete production has justified the efforts that the research community has made in the last decades. All the techniques developed in this nanotechnology field have as their main purpose the manipulation of concrete´s structural composition in order to improve the performance of bituminous and cementitious products. These improvements have been achieved, to a great extent, by the addition of NPs in cement and concrete´s matrix constitution. To the author´s knowledge the most effective NPs for concrete production are:

- Nano-silica and silica fume
- Titanium dioxide
- Iron III oxide
- Chromium III oxide
- Nanoclay
- Calcium carbonate
- Alumina

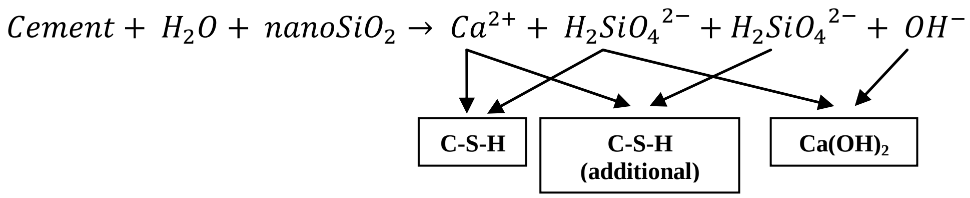
- Carbon nanotubes
- Graphene oxide

The following sections summarize the recent progress in the nano-modification of cement-based materials and their influence on concrete behaviour.

2.1 Nano-silica and silica fume

Regarding the application of nanotechnology in concrete, Nano-Silica (NS) or silicon dioxide (SiO_2) and its colloidal form named as Silica Fume (SF) have attracted considerable attention from the scientific and technical communities. Their remarkable properties justify the large number of studies that have been carried out in the last years (Allen and Livingston, 1998; Hooton et al., 1996; Sabir, 1995). In fact, the application of SF has been extensively reported in the research community with proved results and effective implementation. The advantages of using SF include high early compressive strength, high tensile, flexural strength and modulus of elasticity, enhanced durability, low permeability, among others. For example, Behnood and Ziari (2008) reported improvements up to 25% in compressive strength for heat and unheated specimens with 10% wt% cement replacement. Igarashi et al. (2005) evaluated the capillary porosity and pore size distribution in high-strength concrete containing 10 wt% of silica fume at early ages. It was concluded that concrete with SF has fewer coarse pores than ordinary concrete, thus a reduction of porosity was observed due to the micro dimension of these particles. Taking advantages of these potentialities of the use of SF, its application in the production of high-performance concrete for highway bridges, parking decks or marine structures was analysed (Siddique, 2011). The opportunity of applying nanotechnology resulted in a rise of interest on the application of these particles with smaller size in concrete production (e.g. nano-silica).

In concrete, NS and SF may work at two levels. The first level corresponds to the chemical effect triggered by the pozzolanic reaction of silica with Calcium Hydroxide (CH) (Singh et al., 2013). This produces additional Calcium Silicate Hydrate (C-S-H) gel which is the main constituent for the strength and density in the harden binder paste. Figure 2.1 exemplifies this reaction.



$$Cement + H_2O + nanoSiO_2 \rightarrow Ca^{2+} + H_2SiO_4{}^{2-} + H_2SiO_4{}^{2-} + OH^-$$

Figure 2.1 - Production of Calcium Silicate Hydrate (C-S-H) via pozzolanic reaction of silica with Calcium Hydroxide (CH).

Pozzolanic reactivity is highly increased by higher surface area of pozzolanic particles, which then increases the rate of the pozzolanic activity (Chong et al., 2012). The second level is a physical effect because NS is about 100 times smaller than cement. It can (i) fill the remaining voids in the young and partially hydrated cement paste, (ii) increase its final density, (iii) reduce its porosity and permeability and (iv) decrease the weight of cement used in the mix (Quercia and Brouwers, 2010).

The published experimental results reflect how the inclusion of these NPs may influence the mechanical and durability properties of concrete, and a lot of work has been done in this field. Rashad (2014) presented an extensive overview about the effect of NS on the main properties of traditional cementitious materials and alkali-activated fly ash. The use of NS in concrete production has a high potential to improve a wide range of fundamental properties in concrete, such as (i) strength, (ii) workability and setting time, (iii) heat of hydration, (iv) fire resistance or leaching and behaviour under aggressive environments.

Regarding concrete strength, it has been shown that compressive and flexural strength may increase up to 75% with the addition of small amounts of NS (0-10%). Shakhmenko et al. (2013) tested the effect on cement paste's mechanical properties of replacing cement with different amounts of SF and NS. A cement/SF paste at 2% of cement mass sample was prepared and different samples of 2% of cement mass of SF and NS non calcined (HF0), NS calcined at 400 ºC (HF400) and NS calcined at 1000 ºC (HF1000) were tested. The results showed that mixes containing SF and SF compositions with NS particles demonstrated higher values of compressive strength (more than 3 times higher at early ages and approximately 15% at 28 days) and long-term hardening effect compared to pure cement paste (CEM). These higher values of compressive strength occur at all ages of hardening but the differences are clearly visible in the early stages, as shown in Figure 2.2, where the 1-day compressive strength results are summarised. Figure 2.2 shows that the higher value of 1-day compressive strength was 54.0 MPa, obtained for samples with SF and NS calcined at 400 ºC (HF400). The remarkable reduction observed for samples with SF and NS calcined at 1000 ºC (HF1000) is mainly explained by lower specific surface of this sample compared to others, due to the particle melting observed during the calcining process.

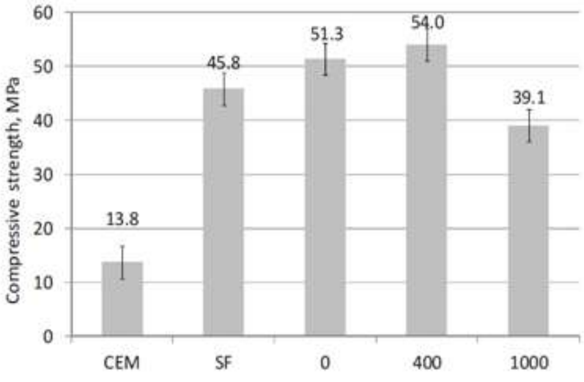


Figure 2.2 - Results of compressive strength in age of 1 day (CEM), paste with SF, paste with SF and HFO NS (HFO) and paste with SF and HF1000 NS (HF1000) (Shakhmenko et al., 2013).

Jalal et al. (2012) tested mechanical, rheological, durability and microstructural properties of high-performance self-compacting concrete (HPSCC) incorporating micro SiO_2 and NS replacing a fraction of Portland cement. Different amounts of 10%, 2% and 10%+2% of micro silica, NS and a blend of micro and NS, respectively, were tested. The w/b ratio was kept constant at 0.38 and different binder contents were tested. It was concluded that the replacement by 2% NS in binary mixes increased the compressive strength for a binder content of 400kg/m^3 by 45%, 55%, 70% and 73% at 3, 7, 28 and 90 days, respectively. Since the effects of NS in these mechanical properties are pronounced, many efforts have been made to establish an optimum content of NS that gives concrete the highest compressive strength. It is almost consensual that, to avoid the agglomeration effect, the percentage of NS in concrete should not be more that 10%. Some authors (Kuo et al., 2006a) reported that 2% is the optimum content of NS, others reported 3% (Qing et al., 2006) and 6% (Qing et al., 2007). However, the results are affected by so many factors such as curing conditions, w/b ratio, NPs size or chemical admixtures, that it is still hard to establish the optimum content (Rashad, 2014).

Apart from strength, using NS in concrete also has high impact on other properties. The addition of NS particles influences hydration behaviour and leads to differences in the microstructure of the hardened paste. A good dispersion of NS particles in the cement mortar led to a denser microstructure and accelerated the hydration process of the cement paste. However, when the low w/b content ratio is used to prepare a mortar or a concrete, internal friction between grains and agglomeration of particles are very intense which leads to poor homogenous dispersion of solid grains in the hardened state of mortar. Figure 2.3 shows a poor dispersion of solid grains in mortar without additions of SF or NS. This microstructural property is highly improved when SF or NS are used. Figure 2.4a and Figure 2.4b show higher levels of dispersion of NS and SF in the matrix and the differences in sizes between them. These differences allow these NPs to fill the voids leading to a denser microstructure.

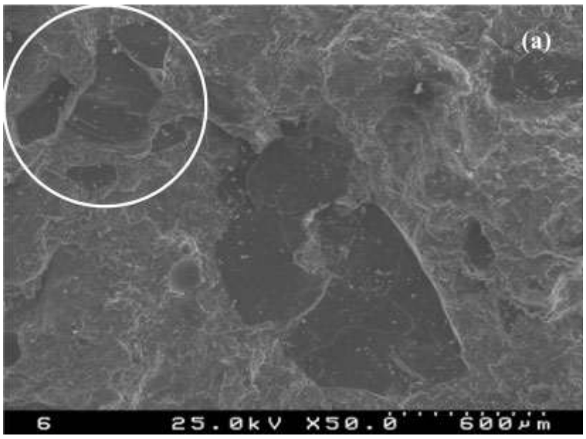


Figure 2.3 - Image (SEM) showing a poor dispersion of solid grains in mortar 0%SF (Senff et al. 2010).

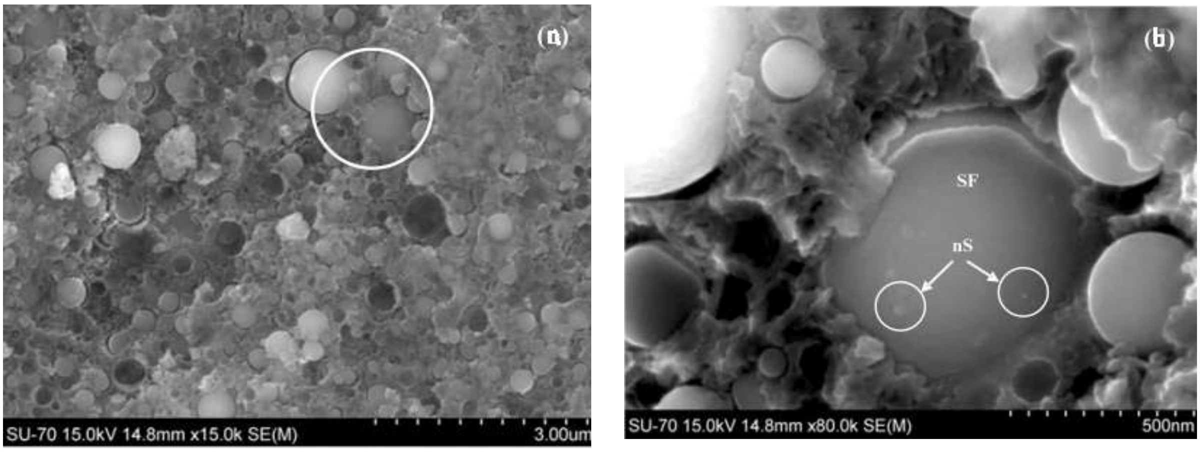


Figure 2.4 - Image (SEM) showing (a) size distribution of SF (nS + SF = 2 + 10.2%) and (b) different sizes between SF and NS (nS + SF = 2 + 10.2%) (Senff et al. 2010).

However, as NPs are easy to agglomerate due to their great surface energy, large quantity of these NPs cannot be uniformly dispersed. In that case it may result in voids and weak zones formation (Singh et al., 2013). Li et al. (2004a) experimentally studied the mechanical properties of nano-Fe_2O_3 (NF) and NS cement mortars. NPs contents in the mortar specimens were 3, 5 and 10% by weight of cement. Apart from an increase of the compressive strength of the specimens, a SEM (Scanning Electron Microscope) comparative study of the microstructure between cement mortars mixed with NPs and plain cement showed that SF and NS filled up the pores and reduced CaOH compound within the hydrates. The texture of hydrates products was denser, uniform and compact which explains the extremely good performance of the products. Hou et al. (2013) tested different samples of cement pastes with and without 5% NS/SF at a w/b ratio of 0.4. The results suggested that the addition of NS increased both the hydration peak temperature from approximately 38ºC to 43ºC implying a higher degree of cement hydration in these pastes. Also the reaction rate increased approximately 30% in comparison with control cement pastes without additions. The increase of the rate of hydration highly depends on the surface area of NS particles added to the mixes. NS particles act as nucleation sites that accelerate the hydration. Since the surface area is higher, so is the rate of hydration. Moreover, workability and fresh properties of concrete also seem to be highly affected by using NS in the mixes. The addition of NS to cement pastes demands more water to maintain its workability (Heikal et al., 2013, Singh et al., 2013). Some authors, such as Bahadori and Hosseini (2012), Berra et al. (2012) and Qing et al. (2006), obtained a remarkable reduction of mixes workability when NS particles were used. Contrarily to this reduction of workability, increased cohesion and yield stress in cement pastes were achieved with NS addition. Superplasticizers have been used to improve the mix´s workability but its quantitative effects on NS reactivity and dispersion of NS particles are still not clear. In fact, the rheological properties of the fresh cement pastes are complex and more studies are needed. Kong et al. (2013) studied the rheological properties of fresh cement pastes with w/c ratio of 0.4 and with 0.5 wt% NP addition. It was suggested that if the water content was kept constant the addition of NS is believed to promote the packing of cement particles decreasing the voids between them and increasing the free water, contributing to fluidity in the paste. However, the decrease of workability obtained by the majority of authors is explained by the fact that not all the agglomerates act as fillers that occupy the void space between cement particles and release free water. In addition to the high water absorption of NS particles, these agglomerates will not only act as fillers but also consume free water that originally contributes to fluidity.

Some authors (Martins and Bombard, 2012; Senff et al., 2010) also suggested that the agglomerates may push away the cement particles around them causing an increase of the void space. This behaviour explains the decrease of workability. Therefore, the influence of NS addition on the rheological behaviour mainly depends on whether the agglomerates can act as fillers or not. Figure 2.5 summarizes this fact. The tests performed suggest that, in most cases, NS agglomeration doesn´t act as filler and cause a decrease in workability. For this reason, including superplasticizers in the mixes should be the best solution, even though more results on this issue are needed.

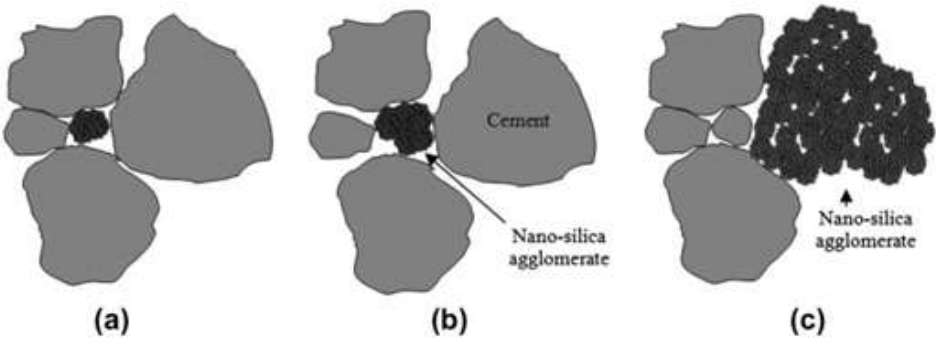


Figure 2.5 - Illustration of the filling effect of NS agglomerates: (a) The smaller agglomerates act as fillers to release some free water in the gap to enhance the fluidity of the paste; (b) The larger agglomerates cannot act as fillers; they tend to push away the particles around them, resulting in an increase of the void space; (c) The very large agglomerates absorb some free water originally contributing to the fluidity of the paste (Kong et al., 2013).

Finally, the addition of NS particles to cement pastes also has consequences on other properties less crucial to concrete structural performance, such as thermal behaviour, abrasion resistance or calcium leaching. Concerning the thermal behaviour, the NS addition to cement pastes significantly improves the thermal stability of the cementitious systems exposed to temperatures of 500ºC with lower strength loss. Related to this, Ibrahim et al. (2012) studied the performance of cement-based materials under temperatures of 400ºC and 700ºC where cement was replaced by high-volume fly ash combined with colloidal NS. A constant w/b ratio of 0.4 was established and the NS/binder ratios were 2.5%, 5% and 7.5%. The results showed an increase of approximately 30% and 20% in both the compressive and the flexural strength of samples with the addition of NS before exposed to high temperatures. This rise was also observed as the NS content increased. After exposure to 400ºC, an increase of 70% in the compressive strength for 28-days was observed when NS was used. Contrarily, the flexural strength decreased about 10% after this exposure. When exposed to higher temperatures (700ºC), a dramatic decrease in both compressive and flexural strength (30% and 80%, respectively) was observed.

Furthermore, several tests (Li et al., 2006a; Nazari and Riahi, 2011a; Shamsai et al., 2012) have been performed to study the abrasion resistance of concrete mixes modified with NS. This property plays a key role in the use of concrete in pavements. The results showed that the abrasion resistance of concrete containing nano-TiO_2 (NT) and NS is significantly improved (100-180%), much more when compared to plain concrete or concrete containing polypropylene fibres (30-70%) (Li et al., 2006a). The relationship between abrasion resistance and compressive strength of concrete also indicates that the abrasion resistance increases with the increasing of compressive strength. For example, an improvement from 30 MPa to 40 MPa in the compressive strength may reduce 25% the depth of wear, from 4 mm to 3 mm.

Besides all the properties' improvements, the environmental and health effects of using NS should also be considered. There are only a few studies about the environmental behaviour and effects of NS. Normally it is reported that NS has very little impact on the environment and its use in the amorphous form is seen as quite safe, in contrast with its crystalline form (Som et al., 2011). The inhalation of crystalline form of NS may induce slight inflammation effects in the lungs. Thus, the toxicity of samples and the risk of exposure to these NPs depend on how the amorphous form of NS is contaminated with crystalline NS. Still, the risk is generally perceived as low.

Considering all aspects, and even if the reasonable cost of NS is taken into account, NS is nowadays one of the most promising and effective nanomaterials to use in concrete production and it is expected to have effective introduction in construction´s industry in the short-term. “Cuore Concrete” reflects this reality with the introduction of NS in concrete production with some of the advantages previously referred. Pascal Maes (2014) presented as main advantages of Cuore Concrete the reduction in the use of cement around of 35-50%, resistance to compression from 40 MPa to 90 MPa in 1 day, 70 MPa to 100MPa (or more) in 28 days in addition to reduced production costs compared to traditional production methods and formulas.

2.2 Nano-Titanium Dioxide

If compared to NS, the application of TiO_2 NPs in cementitious materials is justified by different reasons. It is well known that the cement industry is responsible for the emission of high levels of pollutants, namely nitrogen oxides (NOx) and carbon dioxide (CO_2),, which results in an emerging need for environmental regulations to stimulate the development of new strategies to lessen polluting agents (Cárdenas et al., 2012). In this respect, combining TiO_2 NPs with cement-based construction materials seems to be a good solution, due to its strong photocatalytic activity, which results in (i) an environmental pollution remediation, (ii) self-cleaning and self-disinfection, (iii) high stability and (iv) relatively low cost (Hashimoto et al. 2005). The photochemistry of TiO_2 has become a subject of intense research since Fujishima and Honda (1972) reported the photocatalytic splitting of water on TiO_2 in the 1970s. Since then, the application of TiO_2 photocatalysts to construction materials started to be highly focused (Fujishima et al., 1999).

Photocatalytic activity can be summarised as follows: when exposed to UV irradiation, TiO_2 NPs can absorb photon energy resulting in the promotion of an electron from the valence band to the conduction band of Titania, which generate “holes” (h+, electron vacancy) in the valence band. This electron-hole pairs may recombine in a short term to start redox reactions. These reactions depend on ambient conditions, generating several radicals, such as OH (from oxidation), H_2O_2 or O_2^- (from reduction) when water vapour and oxygen are present around the activated TiO_2. Pollution remediation occurs when these radicals react with harmful substances absorbed on the TiO_2 surface, resulting in the degradation of these substances (e.g. NO_x oxidation) and release of harmless substances such as CO_2 and H_2O, as illustrated in Figure 2.6 (Agrios and Pichat, 2005; Chen et al., 2012).

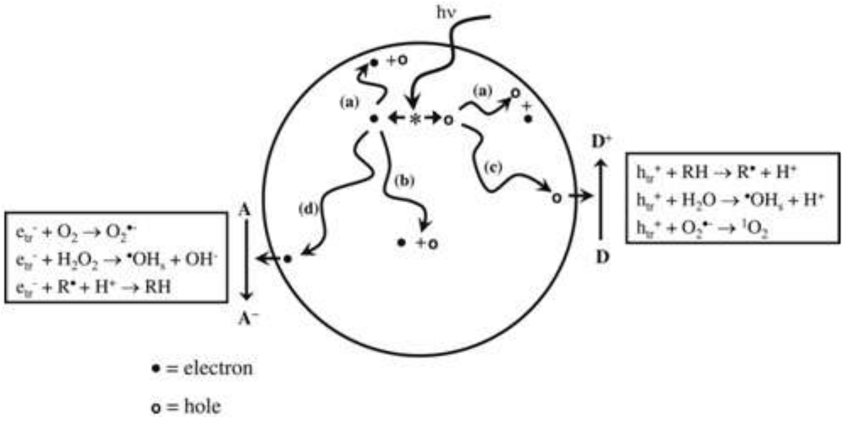


Figure 2.6 - Processes occurring on bare TiO_2 particle after UV excitation (Fujishima et al., 2008).

A self-cleaning effect, i.e. the removal of inorganic substances dirt on surfaces due to rainwater soaking between this absorbed substance and the TiO_2 surface, is obtained by the photo-induced hydrophilicity of the catalyst surface (Folli et al., 2012). Since the photocatalytic activity of TiO_2 is influenced by the (i) crystal size, (ii) crystal structure, (iii) crystallinity and (iv) surface hydroxylation, the use of TiO_2 NPs may increase this activity compared to TiO_2 particles. In this sense, several works have been carried out in order to quantify the consequences of using TiO_2 NPs in NO_x reduction. For example, Cárdenas et al. (2012) studied depollution activity of cement pastes samples, added with 0.0%, 0.5%, 1.0%, 3.0% and 5.0% (of dry cement weight) of TiO_2 NPs, by evaluating NO_x degradation. Different blend ratios of TiO_2 NPs were tested and measurements were made at two aging times, 65 h and 28 days. The results showed that all cement pastes containing TiO_2 NPs had photocatalytic properties, regardless of the ratio and the percentage of TiO_2 used. Moreover, the samples with 5.0% of addition showed the highest photocatalytic activity, both at early and later ages. Senff et al. (2013) designed cement mortar with additions of NS and nano-TiO_2 together. Samples with 0-2wt% of NS, 0-20 wt% of nano-TiO_2, 0.45-7wt% of superplasticizer and 0.45-0.58 w/b weight ratio were tested. Because of nano-TiO_2, NO_x photocatalytic degradation up to 1 h under solar light ranged from 65% to 80%. Lucas et al. (2013) studied the way how microstructural changes affect the photocatalytic efficiency of mortars prepared with aerial lime, cement and gypsum binders with the addition of TiO_2 NPs. The results showed that all compositions exhibited high photocatalytic efficiency, although a decrease of approximately 25% and 30% in the flexural and compressive strength respectively was observed for higher amounts of additions (2.5 wt% and 5.0 wt%). Despite the efforts of the research community to address the advantages of using TiO_2 NPs, the benefits of its use have not being fully validated by field trials, moreover for higher amounts of additions. For example, the Progress Report “PhotoPAQ” (2012) stated that the effectiveness and the real impact on air quality of these new technologies have been demonstrated only in a very limited manner in real-scale applications.

Still and despite some unconformity related to the optimum amount of TiO_2 NPs that should be used to increase NO_x degradation, some products have been introduced in the construction industry such as TioCem (Balte, 2009).

Apart from self-cleaning and NOx degradation, other potentialities of using TiO_2 NPs in concrete have been tested. One of them is related to the potential of mixing TiO2 powders in cement-based materials without additional treatments, due to the porous structure of the hardened cement pastes or mortars (Chen et al., 2012). It was also demonstrated that TiO_2 was inert and stable during the cement hydration process. For these reasons, the application of these NPs may have important consequences on the total porosity and pore size distribution of the cement pastes. Nazari and Riahi (2011b, 2011c) stated that TiO_2 NPs could improve the pore structure of concrete and change the pores size distribution to harmless or slightly harmful pores.

In addition, some research has also been conducted trying to understand the effects of the replacement of cement with nano-TiO_2 on the mechanical and performance properties of hardened cement pastes. Nazari and Riahi (2011b) stated that TiO_2 NPs as a partial replacement of cement up to 3 wt% may accelerate C-S-H gel formation, due to an increase of the amount of crystalline $Ca(OH)_2$ at the early stages of hydration. This resulted in an improvement up to 45% of the compressive strength of concrete.

Their conclusions also showed that an increase of TiO_2 by more than 3 wt% may have the opposite effect. This means that the compressive strength may be reduced due to the decrease of crystalline $Ca(OH)_2$ content required for C-S-H gel formation and unsuitably dispersed NPs in the concrete matrix. Meng et al. (2012) tested different samples of cement mortars with w/b ratio of 0.5 and addition of 5% and 10% of TiO_2 NPs by weight of binder. The results indicated that early strength (1 day) increased by 46% in both samples and decreased by 6% and 9% at 28 days for 5% and 10% of replacement, respectively. These authors concluded that the amount of addition used might have been excessive, causing the decrease at 28 days.

In fact, compared to NS, TiO_2 NPs have less potential to increase the compressive strength of concrete and to accelerate C-S-H gel formation since TiO_2 is not a pozzolanic material. The results showed that the change of pore structure and the improvement of compressive strength could only be attributed to the micro-filling effect of fine powders, acting as potential nucleation sites for the accumulation of hydration products and not the increasing amount of hydration products (Chen et al., 2012; Meng et al., 2012). In that sense, the influence of adding TiO_2 NPs to cement-based materials is much more dependent on the wt% added to the mix, when compared to NS for instance. Certainly, if TiO_2 is added with a non-adequate content, some properties such as compressive strength may decrease.

Finally, the results also shown that the use of TiO_2 NPs improves the resistance to water permeability of concrete when it is mixed in cement pastes, although those improvements were achieved for a maximum replacement level of 2.0 wt% of nano-TiO_2 (Nazari and Riahi, 2011b). Moreover, if these NPs are coupled with concrete with low water-cement ratio, the microstructure in the interfacial transition zones can be improved and, therefore, the amount of strengthening gel, resulting also in a decrease of the water permeability. These results show that the workability and setting time of fresh concrete decreases as the amount of TiO_2 NPs increases. Figure 2.7 shows these reductions based on the work developed by Nazari and Riahi (2011b).

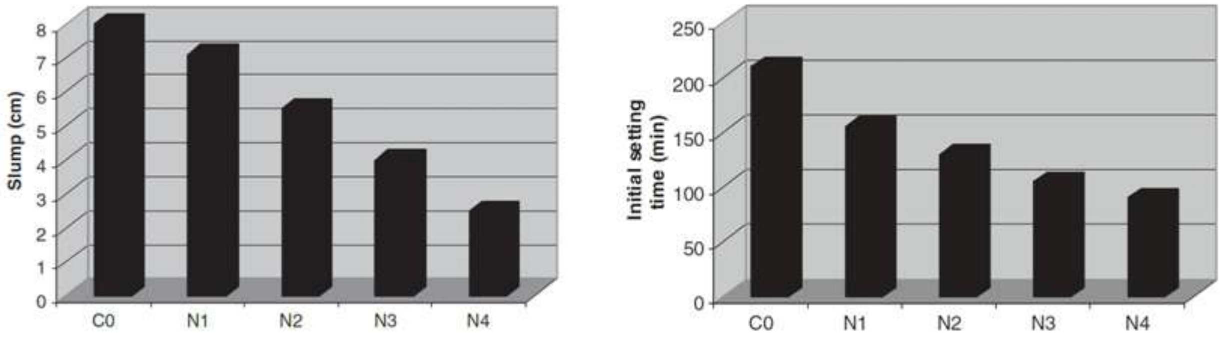


Figure 2.7 - Effect of TiO_2 NPs on: (a) the workability of concrete (b) the initial setting time of cement paste (N1, N2, N3, and N4 are the series N blended concrete with 0.5, 1.0, 1.5 and 2.0 wt% of TiO_2 NPs, respectively) (Nazari and Riahi, 2011b).

Therefore, it is important to identify how the basic properties of TiO_2 NPs modify cement pastes before its application at a large scale, because the amount of TiO_2 in these materials is limited according to their final properties. These aspects have been the object of many studies, aimed to determine the TiO_2

specific amounts that can be more advantageous for the mechanical and thermal properties of concrete (Matějka et al., 2009).

The reasons presented before, as well as the relatively low cost of adding TiO_2 NPs to concrete (when compared to others), justify its application and introduction in the construction industry.

“Self-cleaning” and “depolluting” concrete products with TiO_2 NPs are already being produced and used in some facades of buildings and in paving materials for roads, namely in Europe and Japan (Sanchez and Sobolev, 2010).

One of the most known applications of self-cleaning concrete took place in the ‘‘Dives in Misericordia” church in Rome, completed in 2003 (Figure 2.8). This building was made with 346 prestressed concrete blocks composed by white cement and TiO_2 (binder 380 kg/m and W/B = 0.38) (Cassar et al., 2003).

Figure 2.8 - The “Dives in Misericordia” church, constructed of TiO_2-containing self-cleaning cement (Pacheco-Torgal and Jalali, 2011).

Active monitoring has been done in this building. Six years after its construction there was only a slight change in white colour between the outside surfaces and the inside blocks. There was also some colour variations due to the presence of inorganic substances that easily be completely removed by washing with water (Chen and Poon, 2009).

As mentioned above, other of the main characteristics of the TiO_2 is its photocatalytic property. There are three main application techniques that have been used in order to produce photocatalytic concrete pavements: (i) application of a thin, photocatalyst-containing cementitious layer where the photocatalyst is added as a powder or a suspension during cement making; (ii) application of a photocatalyst-containing solution onto the concrete; or (iii) application by sprinkling the photocatalyst onto the fresh concrete.(Hanus and Harris (2013); Dylla et al. (2011)).

There are also several examples of the application of photocatalytic cementitious materials on roads. In Japan, the application of cement mixtures containing TiO_2 colloidal solutions was used as coating in different roads. One of the test areas, a 300m area on the 7th belt highway in Tokyo (Figure 2.9), presented a reduction of 50-60mg of NO_x per day (Fujishima et al., 2008).

Figure 2.9 - Application of TiO_2 Highway section (the lighter coloured section of the road) (Fujishima et al., 2008).

In China, a section of concrete road on a highway at the Zhonghe Toll station was coated with a solution containing TiO_2 NPs and activated carbon, which penetrated the concrete. The evaluation after three months showed degradation rates of around 37% and 25.84% of NO and NO_2, respectively.

There were also some applications on European countries, such as Italy, Netherlands and Belgium. In Bergamo, Italy, the TiO_2 was applied in area of approximately 12,000 m^2 of road and showed an average day time NOx reduction of 45%. A similar application in Antwerp, Belgium, showed no reduction in photocatalytic efficiency after two years, when washed with distilled water (Hanus and Harris, 2013).

2.3 Iron (III) Oxide

The structural safety of buildings in service is an importance vector in the construction industry. Monitoring and controlling materials and building performance during their life cycle should be guaranteed. For this purpose, several techniques have been used, including embedded or attached sensors that have raised increasing interest. Currently, these types of sensors continue to be the most effective technique to ensure buildings safety. However, the opportunity of developing concrete that can sense its own strain and damage has opened new opportunities. The advantages of producing concrete with self-monitoring characteristics are great: greater durability, absence of mechanical property degradation due to the embedment of sensors and relatively low cost (Li et al., 2004b). In this sense, Iron III Oxide, also known as Hematite, plays a key role. Iron III Oxide is an oxide of iron. Fe_2O_3 has twoiron ions, thus it is called Iron III Oxide. The addition of Fe_2O_3 NPs (NF) may play an important role due to its electrical properties. Several studies have been made in order to evaluate the influence of NF in self-diagnostic ability of stress and damage. Li et al. (2004b) tested different samples of cement mortar with w/b ratio of 0.5 and additions of NF at 3%, 5% and 10% by weight of binder. The results indicated that cement mortar with NF is able to sense its own compressive stress in the elastic and inelastic regimes thanks to their ability to change the volume electric resistance as the applied load changes. Moreover, it has been shown that NF particles do not decrease the resistivity of cement mortar, which is beneficial for the durability of reinforced concrete structure. However, more tests are needed to clearly quantify this influence of NF on the self-monitoring ability.

More specifically, NF may also play an important role in the production of the called heavyweight concrete. This type of concrete is widely used for radiation shielding of nuclear reactors and other structures that require radiation impermeability. Hematite, due to its high unit weight (4.0-4.5 g/cm3), is a potential candidate to be added as a dispersed phase. There are several reports on radiation shielding properties of concrete containing hematite. For example, Gencel et al. (2010) investigated the physical and mechanical properties of concrete with hematite materials, with focus on workability and durability. Regarding the mechanical properties, it was found that there was only a minor effect of hematite added to concrete on its essential properties, namely the compressive strength which did not differ from that of plain concrete. On the other hand, it has been shown that it had high impact on other properties, like shrinkage. With the addition of hematite at 50% by weight of aggregate a decrease of approximately 80% was observed in shrinkage for 15 days. In fact, this is an important property in radiation-shielding concrete. With the reduction of stresses resulting from drying shrinkage, the cracking effect also tends to decrease. However, for 50% replacement, the beginning of segregation was observed, which indicated the use of hematite in smaller contents. Still, the opportunity of using NF for this specific type of concrete should be seriously considered.

Additionally, other tests have been performed in order to assess the influence of NF on other mechanical and rheological properties of concrete, such as water absorption, compressive strength and workability. Nazari and Riahi (2010a) investigated the percentage and rate of water absorption, workability and setting time of binary blended concrete with partial replacement of cement by 0.5, 1.0, 1.5 and 2.0 wt% of NF. The results indicated that the resistance to water permeability increased up to a maximum replacement of 2.0%. Contrarily, the workability and setting time of fresh concrete decreased by increasing the content of NF. Nazari and Riahi (2010b) tested the compressive strength and workability of concrete with addition of NF with average diameter of 15 nm. Different contents were used: 0.5%, 1.0%, 1.5% and 2.0% by weight. The results showed an increase of 15% in the ultimate strength of concrete for a maximum replacement level of 1.0%. Contrarily, the workability decreased with increasing content of NF for a maximum of 8 cm to 3 cm in the concrete slump test, when 2.0% by weight was replaced. Still, more studies are needed on this issue to quantify the influence of NF on the mechanical properties of concrete. In fact, the limited numbers of studies on this issue doesn´t allow to take definitive conclusions on the advantages of using NF in concrete. This fact may be justified by the existence of other NPs with higher positive impacts. Nevertheless, self-monitoring and self-sensing seems to be the property with the best potential advantage concerning the use of NF in concrete structures.

2.4 Chromium (III) Oxide

Chromium III oxide is the inorganic compound of the formula Cr_2O_3. It is one of principal oxides of chromium and is used as a pigment. In comparison with SiO_2 and TiO_2, the use of Cr_2O_3 NPs (NCr) in the cement matrix is referred in fewer studies and, therefore, less results and applications are known. This may be explained by the inherent properties and potential of NCr, which are clearly less appealing than those of other NPs. Nevertheless, there are several reports on the incorporation of these NPs in concrete specimens. The aim of the majority of these studies is to investigate the mechanical properties and water permeability of concrete materials containing different contents of NCr (Nazari and Riahi, 2010c, 2010d, 2011d).

Nazari and Riahi (2011d) tested some samples of concrete with NCr and their results showed that these specimens have higher strength than those without these NPs at every curing age. More particularly, the replacement of cement with NCr with average size of 15 nm up to a maximum limit of 2.0% improved the mechanical properties of concrete, although the optimum level of NCr was achieved for 1.0% for the specimens cured in water where an improvement of 15% in compressive strength at 28 days was achieved. The influence of these NPs on both flexural strength and splitting tensile strength has also been shown. The results showed an increase of these properties in NCr blended concrete when added in the right amounts. For example, at 28 days, for an optimum replacement value of NCr of 1.0%, an increase of more than 50% in the splitting tensile strength was observed. The effects of using NCr are lower in the flexural strength (approximately 5%-10%), particularly for the specimens cured in water. However, these positive effects of NCr may be justified by the additional formation of C-S-H gel in the presence of these NPs.

Similarly to TiO_2 NPs, it was also shown that incorporating NCr in the cement matrix improves other important properties. A reduction of water absorption was also observed in the samples with these NPs. This decrease may result from a reduction of the amount of pores when NCr is added to the cement matrix, due to its filler effect. Thus, the pore structure of self-compacting concrete containing NCr is improved, also increasing the content of all mesopores and macrospores (Nazari and Riahi, 2010d).

Although the advantages of using NCr, important reasons may justify the lack of further research and a slowdown in the investigations and use in construction industry, namely in concrete. On one hand, chromium leaching is known to be a problematic issue to the durability of concrete due to the release of Cr(VI). On the other hand, toxicity concerns have emerged in the last years, which have justified its decreasing use for pigments and paints (Assem and Zhu, 2007). Thus, NCr seems not to be the best option if other types of NPs with similar or higher potentialities are available.

2.5 Nanoclay

Using Nanoclay (NCl) to reinforce cement-based composites has raised much attention to academic and industrial sectors due to the addition of small amount of nanoclay that could substantially enhance the mechanical properties of concrete. Many studies have targeted the applications of clay in cement composites and several enhancements on concrete's properties were achieved. However, fewer studies were assessed to evaluate the effects of the use of nanoclays (NCl) on the mechanical properties and durability of cement based composites. Clay belongs to a wider group of minerals and may be simply described as hydrous silicates (Uddin, 2008). They also can be referred as aluminium phyllosilicates with variable amounts of iron, magnesium, alkali metals and alkaline earths. Clay minerals are characterized by their fine-grained natural structure with sheet like geometry. Individually, natural clay particles are micron and sub-micron in size, and the base structure is composed of crystalline layers of aluminum phyllosilicates with thicknesses in the order of 1 nm. In the literature, clay minerals are divided into four major groups mainly depending on the variation in the layered structure. These include the kaolinite group, the montmorillonite/smectite group, the illite and the chlorite group (Hillier, 2003). Among them, kaolinite group and montmorillonite/smectite group are widely referred when the use fillers in concrete production is studied (Chang et al., 2007; Gaucher and Blanc, 2006; Gruber et al., 2001; Kuo et al., 2006b; Morsy et al., 1997;

Siddique and Klaus, 2009). The kaolinite group has different members, such as kaolinite, dickite or nacrite, each with a formula $\mathrm{Al_2Si_2O_5(OH)_4}$. This means that these members have the same formula but different structures (Uddin, 2008). Contrarily, the montmorillonite group is larger than the kaolinite group and the general formula of its chemical structure is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2XH_2O$. The layer structure contains silicate layers, sandwiching an aluminium oxide/hydroxide layer ($Al_2(OH)_4$).

In the presence of silica and aluminium, clay particles may act as “nuclei” of hydration, possess high pozzolanic behaviour (as well as nano-SiO_2) and can fill the voids in the cement matrix increasing the overall concrete performance. Even if the use of metakaolin (belonging to kaolinite group) (Dhinakaran et al., 2012; Paiva et al., 2012; Siddique and Klaus, 2009) and montmorillonite (Kuo et al., 2006c) particles at micro-scale in concrete production is well reported, nano-engineering in clays is gaining interest in the research community. The large surface area of these NPs and their abundance because of their small size can facilitate the chemical reactions to produce a dense cement matrix with more calcium silicate hydrate (C-S-H) and less calcium hydroxide.

The influence of NCl particles in concrete is mostly related with the mechanical properties, thermal behaviour and microstructure of cement mortars. Morsy et al. (2010) studied the effects of NCl on the mechanical properties and microstructure of Portland cement. Nano-metakaolin (NMK) was prepared by thermal activation to blend in cement preparation. Ordinary Portland cement was used and it was partially replaced by NMK at 0, 2, 4, 6 and 8% by weight of cement. The w/b ratio was established at 0.5. The results showed that the compressive and tensile strength of the cement mortars with NMK was higher than that of plain cement mortar with the same w/b ratio. The tensile strength increased 49% relative to the control mortar and the compressive strength was 7% higher for 8% NMK replacement. Moreover, SEM observations confirmed that the NMK was not only acting as filler but also as an activator to promote hydration process, confirming its high pozzolanic activity (Figure 2.10).

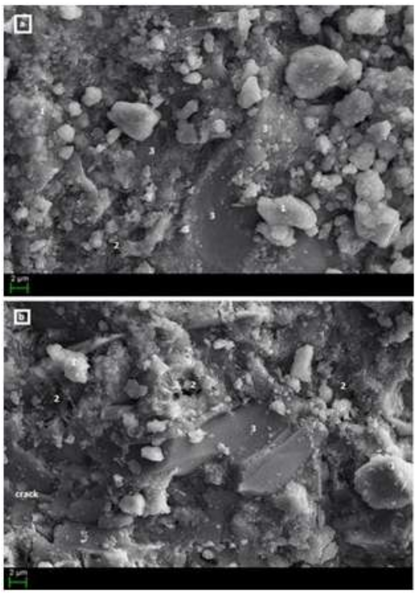


Figure 2.10 - SEM micrographs of (a) nanocomposites containing 1 wt% nanoclay and (b) nanocomposites containing 3 wt% nanoclay. Numbers indicate: 1 = [Ca(OH)2] crystals, 2 = pores and 3= C-S-H gel (Hakamy et al, 2014).

Chang et al. (2007) studied the compressive strength and permeability of the cement paste when nano-montmorillonite is used. Different contents of nano-montmorillonite were used: 0.0%, 0.2%, 0.4%, 0.6% and 0.8% of cement weight. The w/c ratio was fixed at 0.55. Results indicated that, after 28 days, the optimal amounts of nano-montmorillonite were found to be 0.6% and 0.4% by weight of cement, where cement paste composites had the highest compressive strength (20% higher) and the lowest permeability coefficient (25% lower) at 28 days. The impact on the coefficient of permeability was, therefore, higher compared to that on compressive strength. Denser and more stable bonding structures were also found.

Farzadnia et al. (2013) studied the mechanical properties, flowability, thermal behaviour and durability of mortars containing 1%, 2% and 3% of halloysite nanoclay. Halloysite NCl, belonging to the kaolinite group, is a two layered aluminosilicate with predominantly hollow nanotubular structure. Results from its use in mortars showed that the compressive strength and gas permeability of samples improved up to 24% and 56% with 3% and 2% halloysite NCl, respectively.

From the results reported, NCl particles have shown high potential in enhancing the mechanical performance, reducing permeability and shrinkage of concrete in accordance with those of NS. However, the main concern about the use of NCl in concrete is related with an increased water demand of the mix that has to be controlled (Morsy et al., 2011). Clay particles are typically highly hydrophilic, which makes this control an important issue. Moreover, enhanced workability and flowability are needed in concrete production, but without a decrease in its mechanical properties (Sanchez and Sobolev, 2010). Nevertheless, the potential of these NPs in addition to a relatively low-cost may justify further developments in this area.

2.6 Calcium carbonate

Calcium carbonate ($CaCO_3$), or simply NCa, is a common substance found in rocks in all parts of the world, and is the main component of shells of marine organisms. It is created when Ca ions in hard water react with carbonate ions creating limescale. Ground limestone is a sedimentary rock composed largely by calcite and aragonite minerals, which are different crystal forms of calcium carbonate. Ground limestone has been used in the last years to replace part of ordinary portland cement (OPC) in concrete. Energy conservation and natural resources concerns, in addition to ground limestone having lower costs than OPC, justified its use in the concrete industry (Sato and Beaudoin, 2006). A high number of studies have been made in recent years reporting positive effects of NCa addition on different concrete properties, such has the hydration and strength development of concrete (Ali et al., 2013; Ingram and Daugherty, 1991; Péra et al., 1999). The effect on the rate of hydration has been highly focused. It was concluded that the hydration process was accelerated by the addition of finely ground $CaCO_3$ that acts as a nucleation site on which cement hydration products were formed. This micro-physical effect results in a higher development rate of mechanical properties. The introduction of nanotechnology explores the benefits of using NCa with higher surface area, which promotes hydration reactions with relatively reasonable cost. This leads to lower amounts of NCa used with similar, if not enhanced, properties. An increasing number of studies on this issue have been reported in the last few years. Camiletti et al. (2013) tested the effects of NCa on the early-age properties of ultra-high performance concrete (UHPC) with addition of NCa at 0%, 2.5%, 5%, 10% and 15% by weight of cement. The results showed that NCa improved the flowability of UHPC mixes, which also exhibited better workability than other accelerating admixtures. A strong acceleration effect on the early-age setting and hardening process was observed. Moreover, mixes incorporating NCa showed comparable or better early-age compressive strength results, except a high dosage of NCa (>15%) that exhibited a decrease in compressive strength. From the performance and economic viewpoint, it was concluded that adding 5% to 10% NCa was the best choice. Sato and Beaudoin (2010) tested the influence of NCa on the acceleration of hydration of OPC, delayed by the presence of high volumes of supplementary cementitious materials, particularly high volumes of ground granulated blast-furnace slag. Results indicated that the hydration of OPC was significantly accelerated by the addition of NCa: the greater the amount of the addition, the greater was the accelerating effect. The microhardness and modulus of elasticity at the early-stage of the hydration also increased significantly. Admixtures of OPC containing ground granulated blast-furnace slag with 20% NCa addition increased microhardness values from 30 MPa to nearly 140 MPa, close to that of the control OPC at 28 days. The effect is less marked in the modulus of elasticity, but an increase of approximately 10% was observed. Xu et al. (2011) evaluated the effects of NCa on the compressive strength and microstructure of high-strength concrete with standard curing (21 ± 1ºC) and low curing temperatures (6.5 ± 1ºC). The results showed that 1% and 2% of NCa improved the strength of concrete by 13% and 18% with standard curing temperatures and by 17% and 14% with low curing temperature at the age of 3 days.

For these reasons and considering the relatively low cost of NCa compared to other nanomaterials, its introduction in the construction industry is foreseeable, particularly when strength at early ages is very important. However, more research is needed since the study of NCa addition is relatively recent.

2.7 Alumina

Aluminium III oxide (Al_2O_3) is a chemical compound of aluminium and oxygen and it is the most commonly occurring of several aluminium oxides. It is commonly called alumina (nAl) and it has been shown to potentially improve the properties of concrete. It has been stated that using nAl as a partial replacement of cement leads to C-A-S (calcium aluminum silicate) gel formation in concrete, thanks to the reaction of nAl with calcium hydroxide produced during hydration of calcium aluminates (Behfarnia and Salemi, 2013). The rate of this reaction is proportional to the surface area available to react. This possibility justified several studies on the use of nAl with high purity and finesses value to improve the properties of concrete. However, when compared to other NPs, much less studies were reported in the literature. The main reason for this, is the limited effect that nAl has on the compressive strength of concrete. Nazari and Riahi (2011e) tested different samples with different contents of nAl particles with average size of 15 nm. The w/b ratio for all mixes was set at 0.40 and the cement replacement was 0.5%, 1.0%, 1.5% and 2.0% by weight. The results showed that the compressive strength increased approximately 10% with nAl for all ages (7, 28 and 90 days) up to 1.5% replacement and then decreased for values near to those obtained without any addition, although for 2.0% replacement it was still higher than those of the plain cement concrete. Contrarily, Barbhuiya et al. (2014) replaced OPC by nAl powder at 2% and 4% by weight with a w/b ratio of 0.4. Figure 2.11 shows that there are no changes in compressive strength with this addition, especially at the early ages.

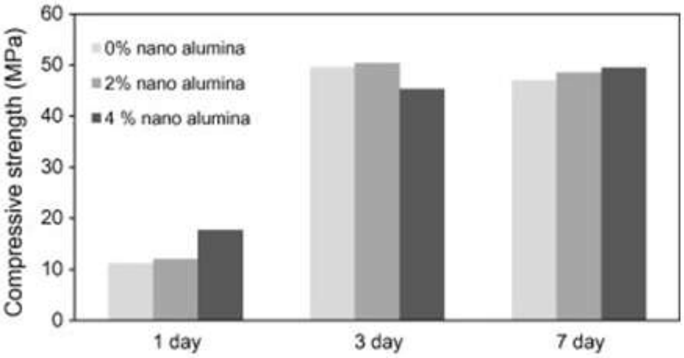


Figure 2.11 - Compressive strength of cement replaced with 0%, 2% and 4% nAl (Barbhuiya et al., 2014).

Behfarnia and Salemi (2013) tested different samples containing 1%, 2% and 3% of nAl by weight of cement with a w/b ratio of 0.48. The results showed a limited increase of compressive strength of 2.6% (7-day), 6% (28-days) and 9% (120-days). Experimental conditions, preparation technology or inadequate mix amounts of nAl may explain this trend (Nazari and Riahi, 2011e).

Despite this limited influence on compressive strength, nAl might have positive effects on other properties, and these possibilities have to be further explored. Li et al. (2006b) investigated the effect of nAl on the elastic modulus of cement composites with various volume fractions (3%, 5% and 7%) with a w/b ratio of 0.4. The results showed that the elastic modulus of composites significantly increased by 143% at 28 days when the nAl fraction was 5%. Moreover, increased compactness interfacial transition zone (ITZ) and decreased porosity were observed. Also, Barbhuiya et al. (2014) observed a much denser microstructure with the addition of nAl to the cement matrix. Its addition also decreased the water absorption and chloride penetration, improving the durability of concrete. Even so, more studies are needed to clearly quantify the effects of the use nAl particles on concrete properties. This will be a major challenge in the near future.

2.8 Carbon nanotubes

Carbon nanotubes (CNTs) are probably one of the most promising materials of the 21st century, due to their higher mechanical properties compared to all other types of nanomaterials.

Their applications are innumerous, either from biology to chemistry or from electronics to medicine. Clearly, the construction industry may be added to these research areas. Within this scope, CNTs have been introduced in several types of matrices (polymeric, metallic, cementitious) and produced an improvement of the mechanical properties of structural materials (Chaipanich et al., 2010; Soliman et al., 2012). In fact, the CNT properties justify such a wide application.

CNTs are tubular nanostructures with a diameter of a few nanometers and a large length/diameter aspect ratio. Its atomic structure consists of a single or several concentric hexagonal lattices of carbon atoms linked by sp^2 bonds and separated by 0.34 nm. Three main techniques were reported in CNT production: arc-discharge, laser ablation and catalytic growth (Popov, 2004). Due to the hexagonal lattice and sp^2 bonds between carbon atoms, CNTs have highly advantageous properties. It is widely accepted that CNTs have a Young modulus around 1.0 TPa (Sinnott and Andrews, 2001), which is five times higher than that of steel (Silvestre et al., 2012), and a tensile strength around 50-100 GPa. In research, two types of carbon nanotubes were reported: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), whose differences remain mainly in their overall thickness (Figure 2.12).

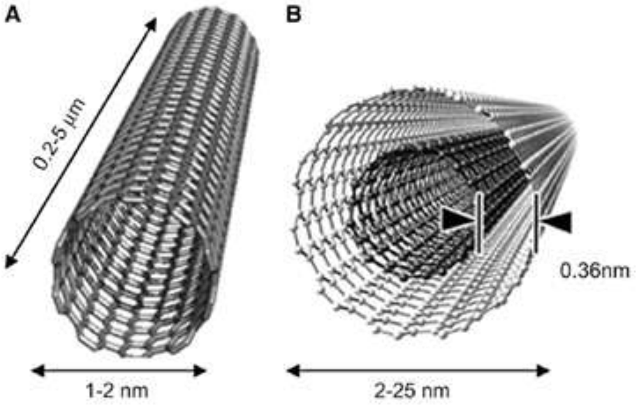


Figure 2.12 - Conceptual diagram of single-walled carbon nanotube (SWCNT) (A) and multi-walled carbon nanotube (MWCNT) (B) delivery systems showing typical dimensions of length, width, and separation distance between graphene layers in MWCNT (Reilly, 2007).

It has also been shown by Faria et al. (2011) and Silvestre (2012) that CNTs only exhibit these impressive mechanical properties under tensile loading. If submitted to compressive loading, twisting or combinations of both, CNTs buckle locally and their stiffness and strength decrease (Figure 2.13). Compared to SWCNTs, MWCNTs seem to be more heterogeneous and their characterization and study are more complex. Furthermore, theoretical calculations and experimental results on SWCNT show that this type of CNTs has more desirable mechanical, thermal, photochemical and electrical properties (Lam et al., 2006). For instance, MWCNTs are slightly lower in strength and stiffness than SWCNTs. However, MWCNTs are (i) less prone to buckling phenomena because of van der Waals forces between different tube walls and (ii) also less expensive and easier to produce with its multiple walls, which certainly justifies their wider applications in strengthening other materials (Soliman et al., 2012).

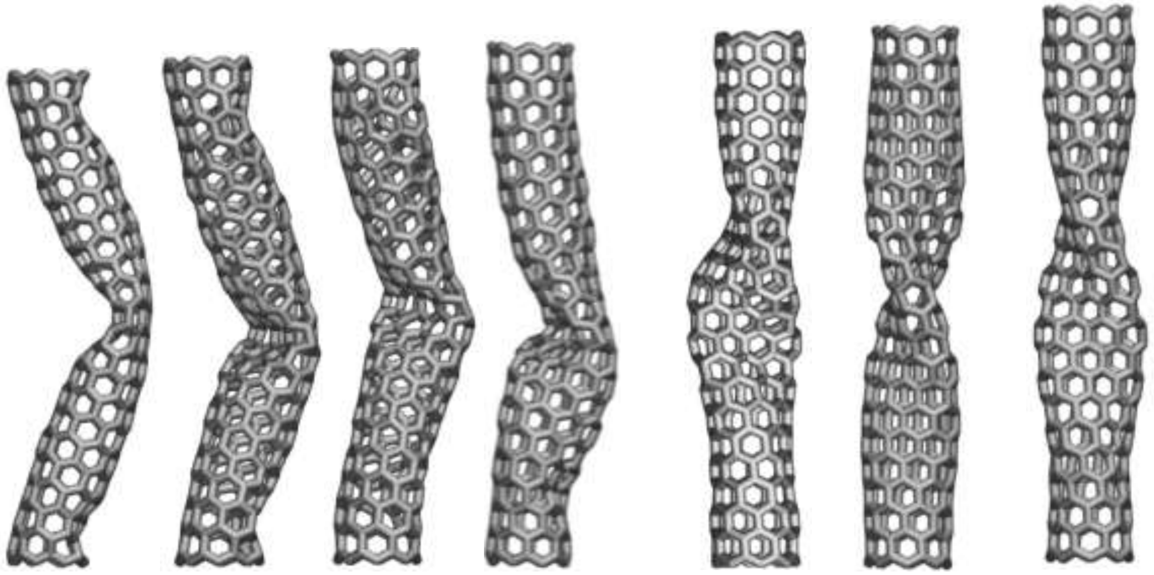


Figure 2.13 - Collapse modes of CNT submitted to several twisting-compression rates (ϕ is the twist in rad; u is the shortening in Å; $\Delta\phi/\Delta u$ is the rate in rad/Å) (Silvestre et al, 2012).

The high aspect ratio of CNTs might be responsible for nanocracks decrease and, therefore, demand higher energy for crack propagation. Moreover, due to the small diameter of CNTs, fiber spacing is also small and a uniform dispersion of CNT is achieved (Konsta-Gdoutos et al., 2010a) if. Depending on their specific structure, these nano materials can be either metallic conductors or semiconductors (Li et al., 2005). Thus, CNTs can also be used to increase the conductivity of the composite material.

An important aspect in the study of addition of CNTs for mechanical improvement of materials is their dispersion in the reinforced matrix. In fact, the effective use of CNTs in nano composites depends on the ability to disperse CNTs within the matrix without reducing their aspect ratio. In order to overcome this problem, many mechanical/physical methods were developed in the last few years. These techniques range from ultrasonication to surfactant addition, from high shear mixing to melt blending or even chemical modification through functionalization. For instance, Li et al. (2005) proposed a H_2SO_4 and HNO_3 mixture solution where multi-walled CNTs were added. Soliman et al. (2012) have used MWCNTs dispersed in a styrene butadiene rubber (SBR) matrix before mixing the matrix with cement, also adding surfactants that have successfully enhanced the dispersion and functionality of MWCNTs in SBR. However, some of these techniques have a high aqueous content, corresponding to the mixing water. Because of this, Metaxa et al. (2012) presented a method to prepare highly concentrated MWCNT suspensions that result on a reduction of the admixture’s volume required in cement-based materials. This method is based on a centrifugal process that can reduce the quantity of water of suspensions (Figure 2.14).

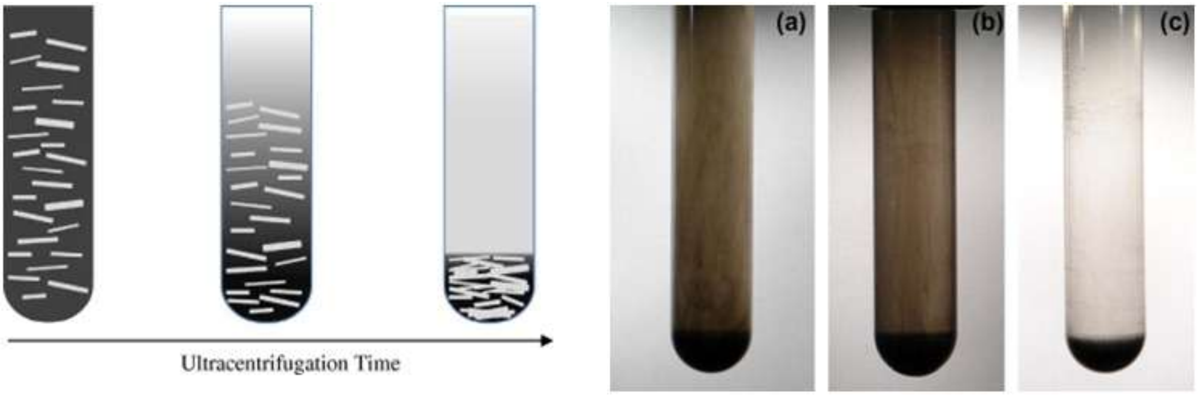


Figure 2.14 - (a) Schematic figure showing the progress of sedimentation of nanomaterials inside a tube during ultracentrifugation (Metaxa et al., 2012). (b) - MWCNTs suspensions ultra-centrifuged for: (a) 30 min; (b) 45 min; (c) 60 min (Metaxa et al., 2012).

The results showed an increase of the concentration of the MWCNT suspensions by a factor of five, with the application of this method. In this way, the dilution of these highly concentrated MWCNT suspensions in nanocomposites results in materials with similar properties when compared to samples prepared using non-concentrated suspensions. This method has the additional possibility of being used in large-scale production of MWCNT admixtures for cementitious materials.

Based on these important aspects about the general properties and applications of CNTs, several results have been presented concerning their addition to cement-based materials. One of the most reported studies is related to the increase of the compressive and flexural strength of fly ash mortars and Portland cement, cement paste or all other cement composites (Chaipanich et al., 2010; Sanchez et al., 2009; Soliman et al., 2012). An explanation for this behaviour is that the functionalized CNTs could provide bond between the COOH groups of nanotubes and the calcium silicate hydrate phase (C-S-H) of the cement matrix, which enhanced the stress percolation, thus increasing the load-transfer efficiency from cement matrix to the reinforcement (Chaipanich et al., 2010). Some investigations on the reinforcing effect of MWCNTs in a cement matrix (w/c = 0.5) suggested that the cement paste matrix reinforced with CNTs can increase its flexural strength and Young's modulus by 25% and 50%, respectively (Konsta-Gdoutos et al., 2010b; Metaxa et al., 2009; Shah et al., 2009). More particularly, Konsta-Gdoutos et al. (2010b) found that small amounts of well dispersed MWCNTs (0.025–0.08 wt% of cement) can highly increase the strength and the stiffness of the cementitious matrix (25-30%). However, the majority of the results presented show lower values of flexural strength and Young's modulus enhancement (10-25%) (Habermehl-Cwirzen et al., 2008).

Nanoindentation results also suggest that MWCNTs can strongly modify and reinforce the nanostructure of cementitious matrix, thanks to a higher amount of high stiffness C-S-H and a decrease of nanoporosity. In fact, some techniques such as SEM micrographs showed good interaction between CNTs and cement matrix, with CNTs functioning as filler. These results on a denser microstructure and higher strength when compared to cement composites without CNTs, are mainly due to the small diameter of these nanotubes that reduces the number of fine pores. However, the strength of fly ash cement mixes is lower than that of Portland cement, because of lower strength development in fly ash cement related with its long-term pozzolanic reaction (Chaipanich et al., 2010).

In this review, it is also important to refer some drawbacks in the success of CNT reinforcement, i.e. research works in which improvement was not achieved. Musso et al. (2009) reported that flexural and compressive tests performed on cement composite with addition of functionalized CNTs showed a significant performance decrease when compared to plain cement. Sáez de Ibarra et al. (2006) also obtained samples with worse mechanical properties than the plain cement paste, especially when no CNTs dispersion method was used. This behaviour is justified by the fact that CNT are so intrinsically hydrophilic that they absorb most of the water contained in the cement mix, influencing negatively a proper hydration of the cement paste.

CNTs can also increase the conductivity of cementitious materials, adding to the fact that cement-based materials are also piezoresistive which means that excellent sensors can be produced for cement structures monitoring. These sensors can easily sense micro-cracking and failure (Azhari and Banthia, 2012). In this context, some studies have been presented showing how advantageous the addition of CNTs can be. Li and Chou (2004) used SWCNT-based sensors in order to measure strain and pressure at the nanoscale. In fact, CNTs change their electronic properties when subjected to strains. Using this strain sensing characteristic of CNTs, it is possible to develop excellent sensors to measure these particular properties (Dharap et al., 2004). The results indicate that the resonant frequency shift is linearly dependent on the applied axial strains or transverse pressure which suggests the potential of such films for multidirectional and multiple location strain sensors in the macroscale.

Nevertheless, much work is still needed to fully understand and evaluate the benefits and potentialities of CNTs in cement composites. There is still a lack of studies establishing the optimum values of CNT and dispersing agents in the mix design parameters, although research in this direction is under progress - see the work by Yazdanbakhsh and Grasley (2012). In fact, it would be expected an enhancement in cement composites performance if better dispersions of CNTs in the cement paste were achieved (based on surface treatment of CNT, optimum physical blending or the use of surfactants). In that sense, Collins et al. (2012) reported the results of several investigations on the dispersion, workability and strength of CNTs aqueous and CNT-OPC paste mixes. These mixes were produced with and without various dispersants compatible as admixtures in the manufacture of concrete, such as butadiene rubber or polycarboxylates. All of these composites were tested and a broad range of workability responses was measured with the main objective of achieving results for CNTs dispersion in hardened pastes.

2.9 Graphene oxide

Graphene is a two-dimensional, crystalline allotrope of carbon. In graphene, carbon atoms are packed in a regular sp2-bonded hexagonal structure, with a C-C bond length of 0.142 nm. A SWCNT can be viewed as graphene sheet rolled into a cylindrical shape to form the tube. Graphene may be viewed as a one-atom thick layer of graphite. On the other hand, graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm. While graphite is a three-dimensional carbon based material made up of millions of layers of graphene, graphite oxide is a little different. By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure which not only expand the layer separation, but also makes the material hydrophilic. This property enables the graphite oxide to be exfoliated in water using sonication, ultimately producing single or few layer graphene, known as graphene oxide (GO). The main difference between graphite oxide and GO is, thus, the number of layers. While graphite oxide is a multilayer system, in a GO dispersion a few layers flakes and monolayer flakes can be found.

One of the advantages of the GO is its easy dispersability in water and other organic solvents, as well as in different matrixes, due to the presence of the oxygen functionalities. This remains as a very important property in order to improve their electrical and mechanical properties. On the other hand, in terms of electrical conductivity, GO is often described as an electrical insulator, due to the disruption of its sp2 bonding networks. In order to recover the honeycomb hexagonal lattice, along with the electrical conductivity, the reduction of the GO has to be achieved. It has to be taken into account that once most of the oxygen groups are removed, the reduced GO obtained is more difficult to disperse due to its tendency to create aggregates.

Graphene oxide (GO) is probably the most prominent nanomaterial whose application in construction industry should be taken as a very meaningful research field in the next years. In fact, its application in reinforcement of concrete for structural applications is still to be reported, although the first steps have already been taken. Like other nanomaterials, GO has a large theoretical specific surface area (2630 m^2/g) and high Young’s modulus (around 1 TPa), similar to that of CNTs. In addition, it also has high thermal conductivity and excellent electrical conductivity, which results in a broad range of potential applications (Zhu et al., 2010). For example, taking advantage of its thermal and electrical conductivity properties, Wang et al. (2008) proposed a transparent, conductive, and ultrathin graphene films, as an alternative metal oxides window electrodes for dye-sensitized solar cells. That is indeed the most studied application of GO in the construction industry, although much more work has been done in other science fields, such as that of chemistry and biomedical engineer (Dreyer et al., 2009). However, Duan (2012) developed a novel method to reinforce concrete construction materials based on the incorporation of GO in a cementitious matrix, resulting in an enhancement of its strength and durability. Figure 2.15a shows that only 0.05% of GO incorporation in cement matrix improves flexural strength of an OPC matrix around 50% and compressive strength from between 15% and 33%. Figure 2.15b shows also a decrease in total porosity with the addition of these nanomaterials. This technology is owned by Monash University and is protected by Patent PCT/AU2012/001582.

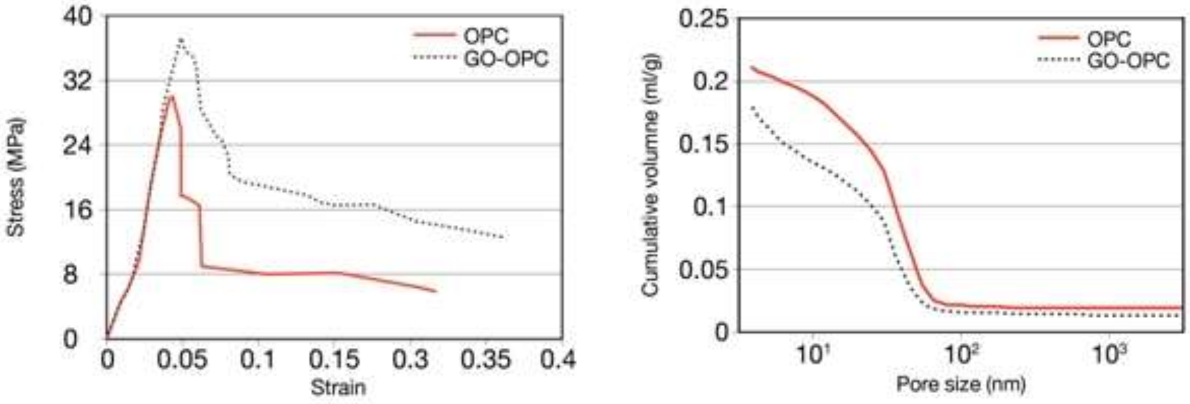


Figure 2.15 - (a) Comparison of mechanical parameters of graphene oxide reinforced cement (GO-OPC) and OPC; the compressive strength of cement paste is 46% higher and (b) the microstructure of cement paste is finer and denser with the inclusion of GO sheets (Duan, 2012).

Babak et al. (2014) synthesized GO using exfoliation of graphite oxide prepared by a colloidal suspension route. They used it to fabricate GO-cement nanocomposites by means of an ultrasonic method and concluded that the use of an optimal percentage (1.5 wt%) of GO nanoplatelets caused a 48% increase in the tensile strength of the cement mortar specimens. Using FE-SEM observation of the fracture surface of the samples containing 1.5 wt% GO, these authors revealed that the GO nanoplatelets were well dispersed and no GO agglomerates were seen in the matrix. Babak et al. (2014) showed the growth of C-S-H gels in GO cement mortar because of the nucleation of C-S-H by the GO flakes. Due to the higher surface energy and the presence of hydrophilic groups on the GO surfaces, the hydrated cement products deposited on the GO flakes acted as a nucleation site. The results by Babak et al. (2014) indicated that the main reason for the observed high bond strength was the nucleation of C-S-H by the GO flakes and its formation along them. FE-SEM observation also revealed microcracks in the GO flakes, implying that the GO flakes stretched across microcracks in the mortar (Figure 2.16a). The breakage observed indicated that very high stresses were applied to the GO flakes. Because of the theoretical tensile strength of GO flake is very high, more GO flakes are needed to carry stresses. The tensile strength of specimens containing 2 wt% GO flakes was much less than that of the control samples, because GO is hydrophilic enough to absorb most of the water contained in the cement mortar, (i) hampering the proper hydration of the cement mortar and (ii) making dispersion of the GO within the matrix difficult. This hypothesis raised by Babak et al. (2014) was confirmed by the 24.7% increase obtained in the tensile strength of specimens containing 2 wt% GO at a water/cement ratio of 0.5 compared with that of the sample containing 2.0 wt% GO at a water/cement ratio of 0.4 (Figure 2.16b).

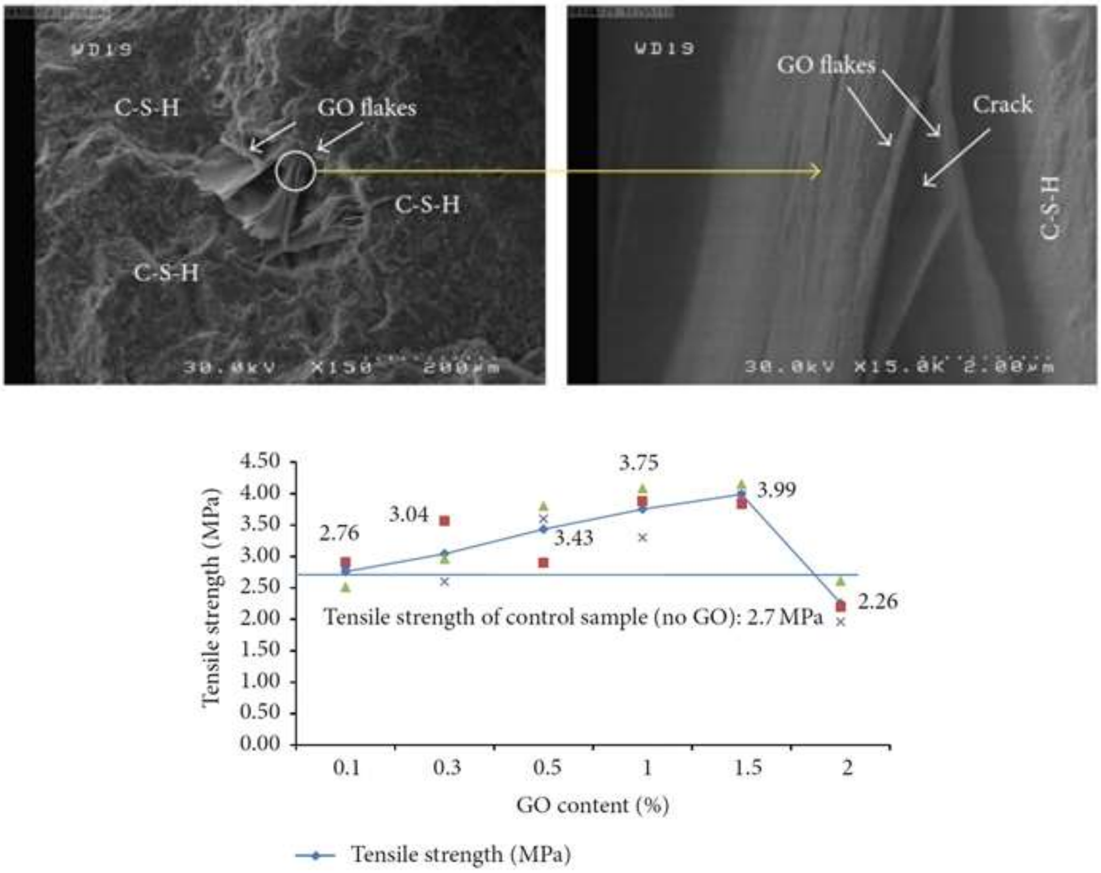


Figure 2.16 - (a) FE-SEM images of cement mortar containing 1.5 wt% GO at scales of 200 and 2.0 μm after 28 days curing, showing microcracks on a GO flake under tensile stresses (b) Tensile strength results of cement mortar specimens with GO content (Bakar et al., 2014).

Although much work remains to be done in developing reliable characterization of GO-reinforcement of concrete and studying rigorously its mechanical properties, the unambiguous advantages of GO increase the expectations of further developments in concrete technology and its future structural applications.

2.10 Concluding remarks

Having presented some of the most relevant and recent research works that has been carried out on the application of nanotechnology in concrete production, it is possible to conclude that the potential of concrete nanotechnology will certainly be the key to a new construction's paradigm. Concrete production is responsible for high levels of CO2 emissions among many others pollutants. In that sense, the application of nanomaterials in the construction industry should be considered not only to improve the physical and mechanical material properties, but also for environmental protection and energy saving. Experimental techniques have been developed, which made the characterization of material properties easier and reliable. Concerning the nanomodification of cement-based materials, titanium dioxide, nanosilica, nanoclay, carbon nanotubes a graphene oxide are the nanomaterials with higher potentialities. Their advantages may be summarized as follows:

- Enhancement of concrete (compressive and flexural) strength;

- Reduction of the total porosity;
- Acceleration of C-S-H gel formation;
- Enhancement of Young's modulus;
- Environmental pollution remediation, self-cleaning and self-disinfection.

From all the nanomaterials presented, nanosilica seems to be the nanomaterial that more advantageous when production of concrete with high compressive strength is needed. Carbon nanotubes have impressive mechanical properties that can play an important role in this issue, but the high cost of production and use of these nanostructures in concrete prevent massive use in the construction industry. On the other hand, when environmental pollution remediation, self-cleaning and self-disinfection issues are taken into account, titanium dioxide NPs are definitely the nanomaterials with more advantages.

Nevertheless, other nanomaterials have come up in recent research works such as the application of graphene oxide, but its high costs are also an issue barring its introduction in the construction industry. Expectations are that costs will decrease over time, as manufacturing technologies improve and demand increases. It is a challenge to the construction industry to solve production and distribution problems to provide solutions to the general public at a reasonable cost.

Another barrier to a wider implementation of nanotechnology regards health and environmental concerns. The effect of various NMs on the natural environment is a subject of debate within the nanotechnology and environmental research community. Some of the potential problems on this matter include leakage of materials into groundwater, release of materials into the air through the generation of dust and exposure to potentially harmful materials during construction and maintenance operations. Therefore, there are some reasonable concerns about the potential adverse health and environmental effects related to the manipulation and use of NMs. The wide range of properties that make NMs so useful, such as their size, shape and surface characteristics, can also cause potential problems if the material is not properly used. For example, nanotechnology-based construction products may cause respiratory problems to construction workers related with the inhalation of dust and aerosol.

However, beyond the current excitement and all the expectations about the use of nanomaterials in the construction industry, further research results are needed in order to clarify some consequences about the use, production and design that are still not fully understood.

2.11 References

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3. POLYMER NANOCOMPOSITES

The present chapter reviews the literature on the application of nanotechnology in polymer nanocomposites (PMCs). In addition to nanoadditions to concrete or cement, nanotechnology may play an important role in other scopes within the construction industry. In this context, polymer matrix-based nanocomposites (PMCs) have become a prominent area of research and development. The opportunity of applying PMCs in structural reinforcement and rehabilitation of damaged infrastructures as well as working as a new structural material justifies the increasing number of recent studies. In fact, the potential of these materials is very high. While the improvements in mechanical properties in PMCs by nano-modifications are the primary area of interest, several other properties and potential applications are relevant such as barrier properties, flammability resistance or improved electrical/electronic properties (Paul and Robeson, 2008). In this chapter the developments in this area are reviewed and possible future opportunities and trends provided.

The structure of a nanocomposite material may be summarized as follows: multiphasic and heterogeneous solid material with a matrix reinforced by NPs. In the case of a nanocomposite material, at least one of the phases has sizes within the nanometer range (Camargo et al., 2009). As in the case of micro-composite materials, nanocomposites materials can be classified according to their matrix materials, mainly in three different categories: ceramic matrix nanocomposites (CMCs), metal matrix nanocomposites (MMCs) and polymer matrix nanocomposites (PMCs). Concerning the construction industry, PMCs have the advantage of the experience of previous applications and studies. As supported in Chapter one, PMCs offer a great opportunity for development, namely in sustainable construction/green building application because of their efficiency and environmental protection. Moreover, PMCs are already being used in various industries due to their ease of production, light weight and often ductile nature.

Besides the type of matrix, the type of additions used plays a crucial role on the properties of the nanocomposites. The preponderance in the literature of the use of nanoclay in PMCs is changing and other nanomaterials are emerging. For example, several studies (Hu et al., 2008; Soliman et al., 2012a) about using carbon nanotubes in polymeric matrixes have been made and high improvements resulting from their incorporation in nanocomposite materials were reported, namely in terms of the elastic modulus and failure stress of PMCs. Moreover, nanosilica and graphene addition in polymeric matrixes has also been tested and interesting developments were reported.

Compared to extended reviews made in this area, such as Feldman (2014), this chapter offers a different perspective. Instead of focusing directly on the types of construction materials where PMCs have already been tested (e.g. concrete, coatings, adhesives), this chapter is structured according to the main nanoadditions analysed. This choice is justified because it is worth understanding the chemistry and properties of these nanomaterials and then relates them with various possible applications in construction. In this sense and to the authors' best knowledge the most effective NPs to use in PMCs and with potential for the construction industry are:

- Nanoclay;
- Carbon nanotubes;
- Graphene;
- Nanosilica;

- TiO_2.

Other NPs have also been tested (e.g. nanoalumina, zinc oxide) in this context, but the number of works published is not relevant enough to be part of this review.

The following sections summarize the recent progresses in modification of polymeric composites with these nanoadditives, with emphasis on the improvement of the properties obtained and applications in the construction industry, such as concrete, thermal and sound insulation materials, coatings and adhesives.

3.1 Nanoclay

Polymer-layered silicate nanocomposites have earned great attention in the research community because of their high potential to increase a large range of properties, especially when compared to pure polymers and conventional filled composites. For example, high dimensional stability, improved flame retardance and enhanced mechanical properties were registered in several studies. The advantages of using layered silicates as the inorganic phase (reinforcement) in PMCs were discussed since the 90's (Giannelis, 1996; Okada and Usuki, 1995). Since then, much work has been done addressing, on the one hand, the improvements and applications of this type of materials (Amiri et al., 2013; Jo et al., 2008; Pique and Vazquez, 2013; Woo et al., 2008; Zhang et al., 2012) and, on the other hand, the preparation and modelling systems to study the structure and dynamics of polymers in confined environments (Dabrowski et al., 2000; Lee et al., 1998; Sinha Ray and Okamoto, 2003; Vaia et al., 1995). This great interest in studying the structure and dynamics of PMCs is based on the fact that clay has a hydrophilic nature that hinders its use as filler in the polymer matrix. In this sense, clay needs to be modified to become compatible with different polymers. The layered silicates commonly used in the preparation of PMCs belong to the same family of 2:1 layered or phyllosilicates. This means that their crystal structure consists of layers made of two tetrahedrally coordinated silicon atoms bonded to an edge-shared octahedral sheet of either aluminium or magnesium hydroxide (Sinha Ray and Okamoto, 2003). Individually, natural clay particles' size is within the micron and sub-micron scale, and the base structure is composed of crystalline layers of aluminium phyllosilicates with thicknesses in the order of 1 nm. The lateral size of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate. Within this group of phyllosilicates, montmorillonite (Jo et al., 2008; Pique and Vazquez, 2013; Shokrieh et al., 2012) is the most common but hectorite (Wang et al., 2005) and saponite (Sinha Ray and Okamoto, 2003) have also been studied.

Two particular characteristics of layered silicates play an important role when application in PMCs is considered: the first one is the ability of the silicates particles to disperse into individual layers; the second one is the ability to fine-tune their surface chemistry through ion exchange reactions with organic and inorganic cations. These characteristics depend, naturally, on the type of polymer matrix used and the interaction between the matrix and the type of reinforcement. Regarding the ability of the silicates particles to disperse into individual layers, the most common classification of PMCs with nanoclay divides them into three categories: intercalated nanocomposites; flocculated nanocomposites and exfoliated nanocomposites. Differences remain at the level of dispersion of nanoclay particles into the matrix and, thus, of the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not). The characteristics of each category may be summarized as follows (Figure 3.1):

- *Intercalated nanocomposites*: system where polymer has entered the galleries between silicates but has not fully delaminated them into the completely exfoliated structure. Thus, intercalated nanocomposites are normally interlayered by a few molecular layers of polymers. For this reason, there is a considerable interaction between silicate layers that may mitigate the fact that the structure is not completely exfoliated, in terms of resulting material properties (Sinha Ray and Okamoto, 2003; Zerda and Lesser, 2001);
- *Flocculated nanocomposites*: this system mostly has the same structure as an intercalated nanocomposite but some silicate layers are flocculated thanks to hydroxylated edge-edge interaction of the silicate layers (Alateyah et al., 2013; Sinha Ray and Okamoto, 2003);
- *Exfoliated nanocomposites*: in an exfoliated system where the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading (Sinha Ray and Okamoto, 2003).

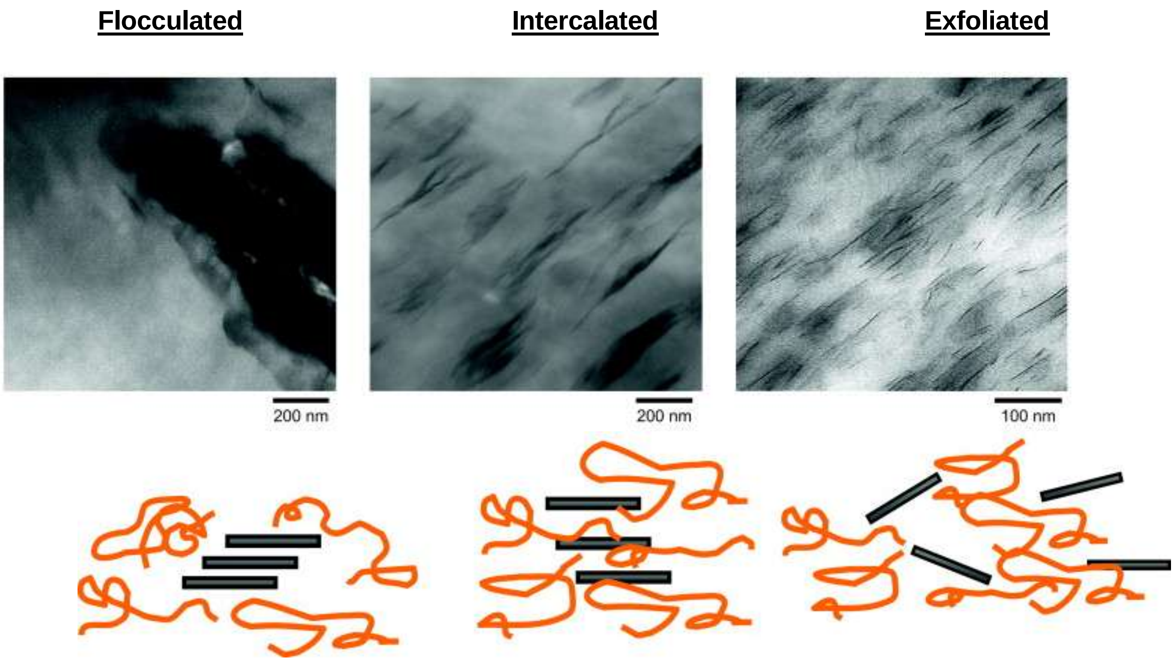


Figure 3.1 - Illustration of various states of dispersion of organoclays in polymers with corresponding WAXS and TEM results (adapted from Paul and Robeson, 2008).

These three types of nanoclay PMCs correspond to different properties of resulting materials, as well as macroscopic appearance. However, true nanocomposites require that the clay nanolayers are uniformly dispersed (exfoliated) in the polymer matrix. Generally, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated structure. Moreover, it has been demonstrated that this type of structure results in a general increase of various properties, such as tensile strength, enhanced barrier properties, thermal stability and flame retardance (Giannelis, 1996; LeBaron et al., 1999; Okada and Usuki, 1995). This could be explained by the fact that a complete dispersion of clay nanolayers in a polymer increases the number of available reinforcing elements to withstand an applied load and deflect cracks. In fact, the high surface area of clay NPs available to interact with polymer matrix facilitates stress transfer to the reinforcement phase, allowing improvements in mechanical properties and temperature behaviour. However, it is very difficult to obtain a completely exfoliated system, depending on many factors: the polymer used in the matrix; the techniques of polymerization applied; the content of reinforcement used. For these reasons, several studies (Barbas et al., 2012, 2013; Gilman et al., 2000; Ngo et al., 2009; Wang et al., 2003) have been performed discussing how to obtain high levels of dispersion of nanoclay platelets into a polymer matrix. For example, Lee et al. (1998) studied the process of intercalation. During intercalation, polymer molecules leave the bulk melt and enter the galleries between the silicate layers. According to the authors, an essential feature of this process is the flow of macromolecules from a bulk fluid to a confined environment. For this reason, a molecular-dynamics simulation of the flow of polymer molecules from the bulk melt into a rectangular slit was performed.

Also the type of polymer used in the matrix plays an important role on the level of dispersion obtained in PMCs with nanoclay. Several polymer-matrix nanocomposites were tested, such as poly-(ε-caprolactone), polyamide 66, polyactide, polyamide 6, polyester, poly(butylene-terephthalate), polypropylene and epoxy resins (Prajapati et al., 2013). From all the tests performed, some interesting results emerged, some with potential application in the construction industry that are presented next. Regarding the deterioration of concrete due to exposure to aggressive environments, Woo et al. (2008) tested the barrier performance of silane/clay nanocomposites as a coating material in concrete structures. The silane/clay nanocomposite was fabricated by curing the silane-organoclay mixture through hydrogen bonding concrete. Two types of montmorillonite-based clay with different organic modifiers were used, namely Cloisite 20A (dimethyl dehydrogenated tallow quaternary ammonium modified) and I.30P (primary octadecylamine modified). Samples with pure Cloisite 20A and I.30P, and 1 wt%, 3wt% and 5wt% silane-Cloisite 20A and silane-I.30P nanocomposites were tested. SEM examination of the coated concrete surface confirmed that the nanocomposite can effectively cover the pores and voids on the concrete surface. A rheological study revealed a linear increase in viscosity with the addition of nanoclay. A moisture permeability test showed that the permeability was reduced by approximately 50% due to the presence of clay of high aspect ratio. It was also concluded that the moisture barrier performance was better for the nanocomposites containing Cloisite20A clay than those with I.30P clay. Approximately 5wt% was found to be the optimal content of Cloisite20A clay that leads to the lowest permeability (50% least). The salt spray test indicated that the application of the nanocomposite coating reduced the average chloride content by 69% compared to the uncoated concrete. On the other hand, Dabrowski et al. (2000) studied the thermal behaviour of both polyamide-6 and polyamide-6 clay nanocomposite. A model of the thermal degradation of both polyamide-6 and polyamide-6 clay nanocomposite was proposed. The role played by oxygen during thermal degradation was also investigated. The results showed that protective barriers are formed during thermal degradation that slow down the degradation rate via a diffusion process, which is approximately four times lower under high temperatures (700K-750K) in the case of polyamide-6 clay nanocomposite. The formation of this protective barrier may correspond to a change phase of the nanocomposite, from a delaminated (exfoliated) structure to an intercalated structure. It was also concluded that oxygen plays an essential role on the stabilization process of nanocomposite.

Scarfato et al. (2012) tested the effectiveness of nanocomposite surface treatments as protective systems for concrete substrates. Organomodified montmorillonite were used in two commercial resins: a coating and a pore line with 2wt%, 4wt% and 6wt% addition. They were applied on concrete substrates and characterized to evaluate their protection performance relative to the plain resins. There was a decrease in porosity of more than 10% of samples with 4wt% Cloisite 30B. Moreover, experimental data showed that the barrier properties to water vapour remain unchanged after the application of the plain resins, but they increased up to 30% using nanocomposites systems. This shows the efficacy of nanofillers in increasing the moisture penetration resistance of the treated substrate. These results open the possibility of using PMCs with nanoclay in coatings and adhesives with better performance under fire conditions and corrosion protection compared to polymer materials currently used.

From a structural point of view, PMCs can also be used in some components, like concrete, due to their very good strength to weight ratio. For example, Shokrieh et al. (2012) tested the effects of adding modified nanoclay (Cloisite 30B) on the mechanical properties (tensile, compressive, and flexural strength, and fracture toughness) of epoxy polymer (ML-506). Subsequently, the mechanical properties of polymer concrete (PC) made of nanoclay/epoxy were also evaluated. Cloisite 30B was added at 0 wt%, 1wt%, 2wt%, 3wt%, 4wt% and 5wt% relative to the epoxy resin. Concerning only the epoxy/nanoclay PMC, Figure 3.2a and Figure 3.2b show an increase of 13% in the tensile modulus for a content of 4 wt% and a decrease of 20% in the ultimate tensile strength for a content of 5 wt%, respectively. Failure strain also dropped approximately 50% from 3.2% to 1.6% for an optimum value of 5 wt% replacement.

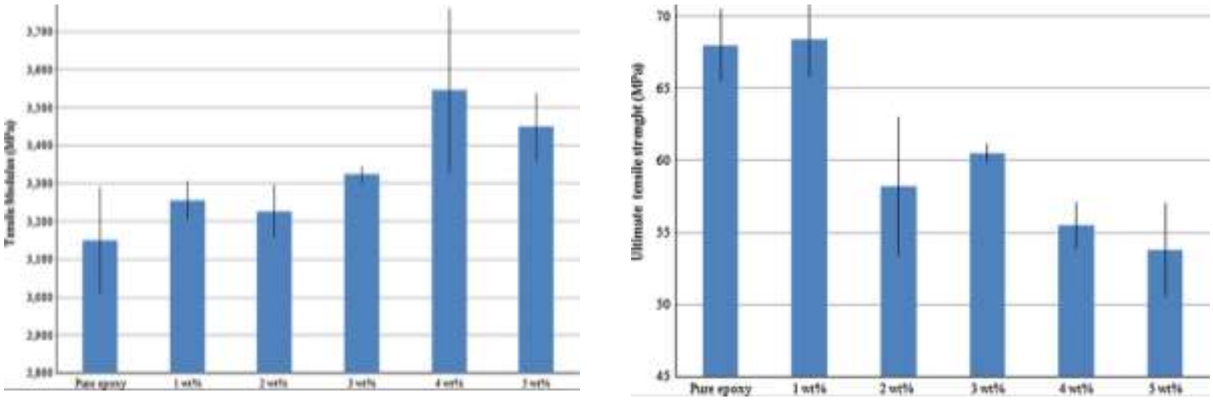


Figure 3.2 – Results of: (a) ultimate compression strength vs. nanoclay content. (b) fracture toughness vs. nanoclay content.(Shokrieh et al., 2012).

Regarding application in polymer concrete composite (PC), Figure 3.3a and Figure 3.3b show an increase in the compressive strength of 15.2% obtained for a 3wt% clay replacement and also an increase of 7.6% was observed in fracture toughness for an optimum value of 5 wt% replacements.

Jo et al. (2008) also investigated the mechanical and thermal properties of montmorillonite with unsaturated polyester matrix (MMT-UP) nanocomposite and its application in concrete. Three types of MMT were used, Na_+-MMT, Cloisite 30B and Cloisite 25A, in samples at 2 wt%, 5 wt%, 8 wt% and 10 wt%. Results suggested that the mechanical and thermal stability of MMT-UP nanocomposites is better than that of pure UP. For example, Figure 3.4a shows that the compressive strength of concrete containing 5%wt Cloisite 30B increased approximately 25%, from 78MPa to 98MPa, at 25 ºC and the modulus of elasticity increased approximately 24%, from 25GPa to 31GPa. Figure 3.4b shows lower improvements for flexural strength, approximately 5-10% at 25ºC (from 24Mpa to 26 MPa). In terms of thermal stability, an increase in temperature naturally led to a loss in strength and modulus of elasticity in the polymer concrete composite specimens because the resin binder’s strength decreased as the temperature increased. However, better performance was registered in specimens with MMT than in those with UP only. For example, for an increase from 25 ºC to 65 ºC, the compressive strength decreased 33% in the samples with UP and 18% in those with MMT-UP. An identical trend was observed for the modulus of elasticity, splitting tensile and flexural strength.

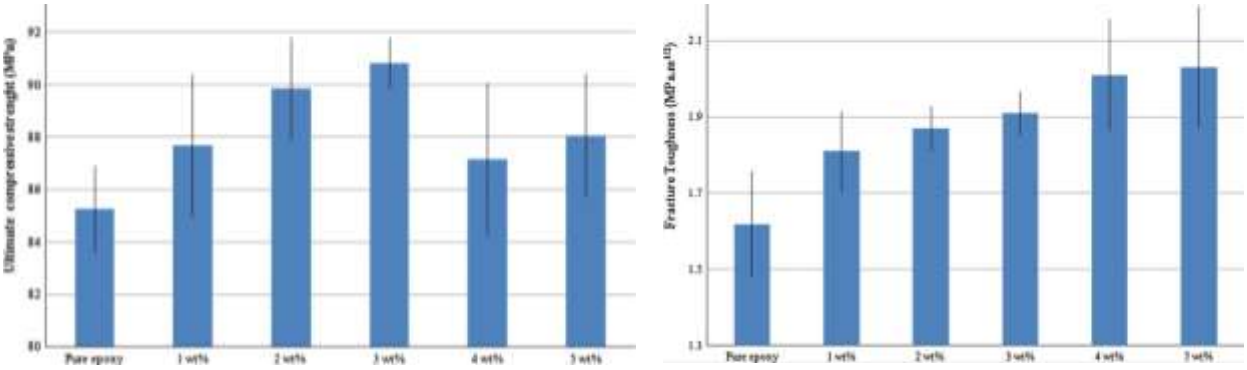


Figure 3.3 - Results of: (a) ultimate compression strength vs. nanoclay content. (b) fracture toughness vs. nanoclay content.(Shokrieh et al., 2012).

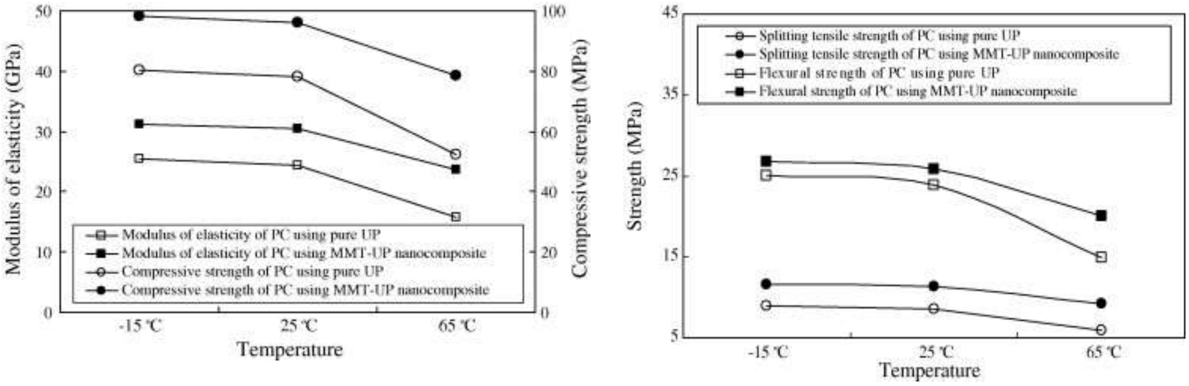


Figure 3.4 – Results of: (a) compressive strength and elastic modulus of polymer concrete using UP-MMT (Closite 30B) nanocomposite. (b) Splitting tensile and flexural strength of polymer concrete using UP-MMT (Closite 30B) nanocomposite (Jo et al, 2008).

The application of PMCs with nanoclays in foams for building construction has also been the objective of various studies. Polymers foams have been used for years but the addition of nanofillers in its production seems to open excellent possibilities of controlling foams morphology and performance (Chen et al., 2013). For example, Cao et al. (2005) tested the properties of polyurethane (PU)/montmorillonite (MMT) nanocomposites foams with organically modified layered silicates (organoclays) by *in situ* polymerization. The presence of nanoclay resulted in an increase in cell density and a reduction of cell size compared to pure PU foam. With the addition of 5% of organically treated clays, an increase of 650% in compressive strength and a 780% increase in modulus of elasticity were observed.

Besides the application of PMCs with nanoclays in buildings, its use in asphalt and bitumen production is widely referred as beneficial to their physical and mechanical properties. (Sureshkumar et al., 2010; Yao et al., 2012; Zhang et al., 2012). For example, Zhang et al. (2012) determined the UV aging properties and microstructures of the SBS modified bitumen, with organo-montmorillonites NPs (Na_+-MMT). Both the viscosity aging index and the softening point increment of SBS modified bitumen as a result of UV aging decreased due to the introduction of NA_+-MMT. Moreover, the micro-morphology of the binders becomes solid-like after UV aging, showing good aging resistance of this type of modified bitumen.

For all the presented reasons, clay-based nanocomposites are the NPs most examined and tested for the construction industry. In addition to mechanical, physical and thermal improvements that they allow, the relatively low price of clay minerals, their availability and their unique characteristics (plate-like morphology with high aspect ratio) clearly justify the interest of the research community. Moreover, a large range of nanoclays is being commercialized for introduction in composites production. For example, Sigma-Aldrich Materials Science, in collaboration with Nanocor Corporation, offers a line of montmorillonite nanoclays to apply in composites production. Table 3.1 shows the application proposed for each product and some of the properties improvements expected with these additions. Depending on the polymer to be modified and the needed property, different products are offered.

Table 3.1 - Nanoclays products for applications in polymer composites commercialized by Nanocor Corporation (adapted from http://www.sigmaaldrich.com/materials-science/nanomaterials/nanoclay-building/nanoclays-montmorillonites.html).

Product Name	Application	Property Improvements
Nanoclay Nanomer ® I.28E	Epoxy (anhydride-cured)	Speed-up cure, improve modulus and chemical resistance
Nanoclay Nanomer® I.30E	Epoxy (amine-cured), polyurethane	Speed-up cure, improve modulus and chemical resistance
Nanoclay Nanomer® I.44P	Polypropylene, polyethylene, ethylene vinyl acetate	Improve modulus, decrease gas permeability, enhance flame and chemical resistance
Nanoclay Nanomer® I.31PS	Polypropylene, polyethylene, ethylene vinyl acetate	Improve modulus, decrease gas permeability, enhance flame and chemical resistance (for higher temperatures applications)
Nanoclay Nanomer® I.34TCN	Polyamides (Nylon 6, Nylon 66)	Improve modulus, decrease gas permeability, enhance flame and chemical resistance
Nanoclay Nanomer® PGV	Hydrophilic polymers (e.g. polyvinyl alcohol)	Improve processing and chemical resistance

However, to make these applications possible, one of the most concerns on using nanoclays in polymer matrices was partially overcome: the dispersion of nanoclays in polymer matrices. These nanoclays products are surface exchanged with cations surfactants, such as alkylammonium cations. The differences between the products mainly remain on the chemical nature of their surface bound cations. In fact, proper dispersion of NPs is the most relevant issue that still need further investigation for wider application.

3.2 Carbon Nanotubes

As referred in Chapter Two, Carbon nanotubes (CNTs) have been extensively looked at by researchers in various fields such as chemistry, physics, materials science, and electrical engineering. Their good mechanical, thermal and electrical properties make them a promising candidate for a wide variety of applications (Popov, 2004; Silvestre et al., 2012; Sinnott and Andrews, 2001). CNTs are tubular nanostructures with a diameter of a few nanometers and a large length/diameter aspect ratio. For this reason, CNTs are often designated as the definitive fibre (nanofibre) for reinforcement of any type of matrix, including the polymeric one, with high levels of dispersion, as shown in Figure 3.5 (Yu et al., 2010). It shows the morphology of 5 wt. % of CNT-filled epoxy adhesive. It can be observed that CNTs are dispersed quite homogenously in the epoxy, with only a few small aggregated bundles enhanced by the mechanical stirring followed by ultrasonication preparation method.

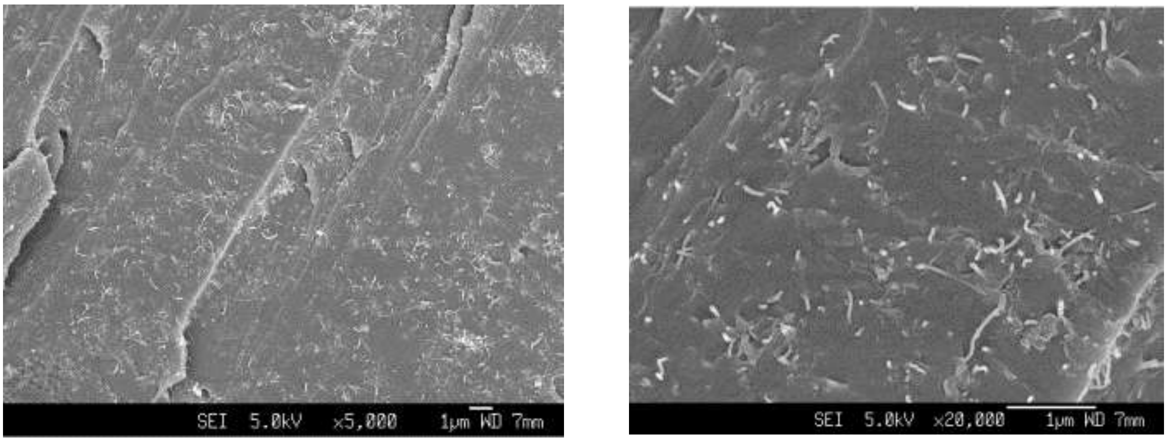


Figure 3.5 - FESEM micrographs of 5 wt.% CNT-filled epoxy (Yu et al., 2010).

In research, two types of carbon nanotubes were reported: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), whose differences remain mainly in their overall thickness (Figure 2.12). Compared to SWCNTs, MWCNTs seem to be more heterogeneous and their characterization and study are more complex. However, theoretical calculations and experimental results on SWCNTs show that this type of CNTs has more interesting mechanical, thermal, photochemical and electrical properties (Lam et al., 2006). For example, MWCNTs have slightly lower strength and stiffness than SWCNTs. However, they have other advantages like being less expensive and easier to produce with its multiple walls, which may justify their wider applications (Soliman et al., 2012b) in strengthening other materials. The construction industry is, certainly, one of the fields where CNTs may play an important role. Within this scope, CNTs have been introduced in several types of matrices (polymeric, metallic, cementitious) and allowed an improvement of the mechanical properties of structural materials (Chaipanich et al., 2010; Soliman et al., 2012b). Structural nanocomposites, in particular, may take advantage of nanotubes' superior mechanical properties as well as their high aspect ratio and surface area. Its application may range from polymer-concrete (PC) systems with addition of CNTs to adhesives and from thermal to electrical insulation materials. Moreover, embedding CNTs in the matrix of composite materials for damping augmentation explained by energy dissipation of these composites has been widely focused. In addition, due to their novel electrical properties, it has been introduced CNTs as outstanding candidates as sensing materials. Therefore, its introduction in PMCs is a realistic alternative to conventional smart materials. PMCs have been reported as sensing materials for various external stimuli, including temperature, pressure, liquid and light. Moreover, CNTs have also been considered as a potential candidate for strains sensors at macroscale, due to the dependence of the electrical properties on mechanical deformation at the nanoscale (Zhang et al., 2013).

Some examples of all scopes of application of CNTs are presented next. In terms of PC, Soliman et al. (2012b) examined the significance of using MWCNTs dispersed in a styrene butadiene rubber (SBR) matrix, before mixing the matrix with cement, to improve mechanical characteristics including compressive and tensile strength and microstructural features. Five mixes were produced in this study: one standard mortar cast prepared according to ASTMC109 standards; one mix contained SBR latex at 15% of the weight of cement; three mixes with 15% of SBR latex and MWCNTs at 0.5%, 1.0% and 1.5% by weight. The addition of CNTs significantly enhanced the failure strain (290%) and the toughness (105%) of the mixes. However, it was observed that MWCNTs did not affect the early age compressive strength. Moreover, the 1.5% MWCNTs addition improved the Young modulus, tensile strength and toughness of SBR films by 135%, 220% and 218% respectively. The improvements were only possible thanks to the good dispersion achieved in this work.

From the perspective of reinforcement of existing concrete structures, Rousakis et al. (2014) studied the tensile testing and mechanical characterization of three epoxy resins reinforced with various concentrations of MWCNTs. The resins are used in crack repair of concrete members as well as in FRP sheet wrapping. Contents of 0.125wt%, 0.25wt% and 0.5 wt% were used to enrich the resins. A remarkable enhancement of their tensile strength (2.25 times that of the host matrix) and deformation at failure (3.27 times that of the host matrix) was reached. Besides the application in concrete, CNTs nanocomposites may play an important role in adhesives production. The behaviour of these materials under high temperatures and the ability to transfer action-effects between the reinforcement and concrete are often weak and CNTs may help to overcome this problem. Soliman et al. (2012a) studied the effect of incorporating various contents of pristine and functionalized MWCNTs on creep of epoxy at the concrete-FRP interface. Pristine and functionalized MWCNTs were at 0.1 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt%. The use of functionalized MWCNTs at the optimum value of 0.1 wt% resulted in a 54% reduction in normalized creep showing the ability of MWCNTs to be used with FRP in strengthening concrete structures to sustain stresses. Kang et al. (2014) compared the static and dynamic strengths of adhesive joints incorporating carbon nanotubes to those without them. Composite to aluminium single-lap joint were fabricated and their strengths were evaluated. With 2 wt% addition of carbon nanotubes, the static strengths of the adhesive joints decreased. Figure 3.6 shows the force-displacement curves of the adhesive joints. It can be observed that the strength of adhesive joints without carbon nanotubes was 4.86 MPa, and with 2 wt% carbon nanotubes were 3.08 MPa. This means that with 2 wt% carbon nanotubes addition the strengths of adhesive joints with 2 wt% carbon nanotubes were about 36.62% lower than those without the carbon nanotubes. However, the fatigue strength was much longer when CNTs were added to the adhesives. Without carbon nanotubes, cracking of the adhesive joint initiated at 1377 cycles and fatigue fracture occurred simultaneously without any crack propagation time. With 2 wt%

carbon nanotubes the crack initiated at 18596 cycles and fatigue occurred at 26297 cycles. This demonstrates the possibility of using CNTs in adhesives not only in concrete structures but also in steel structures (Yu et al., 2010), when the life cycle and fatigue behaviour is concerned.

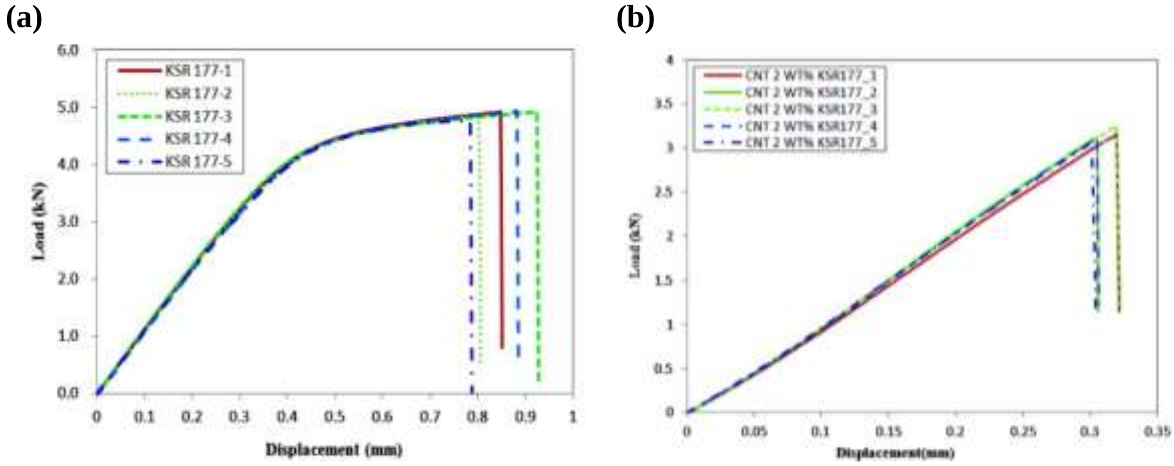


Figure 3.6 - Force-displacement curve of adhesive joint: (a) adhesive without the carbon nanotubes. (b) with 2% wt carbon nanotubes (Kang et al., 2014).

On the other hand, the damping effect of matrix-embedded CNTs in fibre-reinforced composites has been offering the potential to design a passive damping mechanism into functional composite materials. This effect is partially explained by the poor bond that is exhibited between the surface of the CNTs and the surrounding composite matrix, resulting in energy dissipation through an interfacial stick-slip mechanism, since these two surfaces slide over one another under strain (DeValve and Pitchumani, 2014). In fact, if the adhesion between nanotubes and polymer matrices is good, less slippage will occur. Instead, the stiffness increases as result of a good adhesion and better load transfer. Higher stiffness leads to an increase in the natural frequency of the composite. On the other hand, if the adhesion is poor there will be no significant load transfer, and the slippage will increase leading to more dissipation of energy. This fact may have great impacts on the structural performance of different materials, such as composite beams. It is reported that a crack in a structure introduces a local flexibility, reduces the stiffness and may change the dynamic behaviour of the structure. Understanding the vibration characteristics of cracked structures is vital in structural health monitoring and non-destructive damage evaluation (Fan and Wang, 2015). This important property of CNTs has attracted the attention of many researchers. The results obtained are relevant. For example, Koratkar et al (2003) observed approximately 200% increase in damping ratio by addition of 0,05 nano-film of MWCNTs in a piezo-silica composite beam. Rajoria and Jalili (2005) also tested free and forced vibration of CNT-epoxy sandwiched steel beams in order to characterize their stiffness and damping properties in structural vibration applications. Primarily, MWCNTs were found to be better reinforcement choice for damping enhancement. With an optimum value of 5.0% by weight of reinforcement, an increase up to 700% in damping ratio was observed. The relation between the increase of damping ratio and the impacts that the addition of CNTs to polymer matrices has in other mechanical properties has also been discussed. Yeh et al. (2014) measured the Young´s modulus and Poisson ratio of MWCNTs-epoxy composites samples. As

Figure 3.7 shows, there was no significant variation between the different samples for Young´s modulus and Poisson´s ratio. These results suggest that is possible to reconcile the great potential that CNTs have to improve damping properties with the impacts that its addition may have on other mechanical properties, namely Young´s modulus or stiffness.

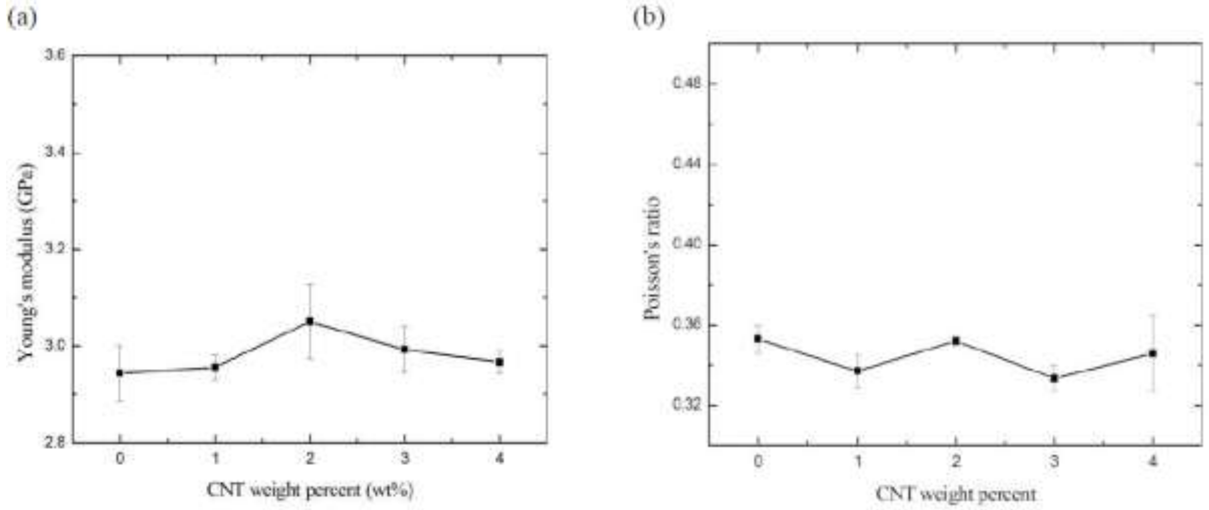


Figure 3.7 - (a) Young´s Modulus and (b) Poisson’s ratio as a function of CNT weight percentage (Yeh et al, 2014).

Finally, CNTs have high potential to be introduced in the production of smart materials (materials with self-sensing abilities). Structures are often exposed to a variety of conditions including impact, shock loading and changes in temperature. Structural health monitoring (SHM) seeks to provide ongoing monitoring of structure´s integrity. Current SHM systems consist mainly in applying a sensor to the outside surface of the structure or in embedding some types of sensors within the composite. These sensors react to strain or other changes in order to detect damages (Sebastian, J. et al., 2014). CTNs with their great electrical properties and sensitivity and if correctly integrated into composite structures may open new opportunities. Many efforts have been made in this direction.

For example, Sebastian et al. (2014) tested different CNTs covered fibre sensors as alternatives to conventional strain gages. Two sets CNTs growth on glass fibre were prepared changing the growth time. As growth time increases, the density and length of the nanotubes on the glass fibre increases with impact on the overall resistance of the sensor. Different specimens for each set were prepared in order to test mechanical behaviour in different orientations, such as uniaxial and orthotropic tension, Poisson and off-axis tension and additional off-axis tension randomly-oriented. Results obtained several trends: uniaxial specimens tests were not consistent with predictions, because it was expected a much higher Poisson´s ratio and, therefore, a stronger lateral contraction that the results suggested. This could be explained by a complex interaction between interlaminar stresses and the CNT conduction mechanism that may justify further work to determine why the sensor does not respond purely due o Poisson effects; tests performed to look at longitudinal, transverse and off-axis response for four sensors simultaneously showed that the sensor aligned with the loading had the highest response, the sensor at 45º to the loading had a lower positive response, and the sensor at 90º to the loading showed a negative response because of Poisson effects (Figure 3.8).

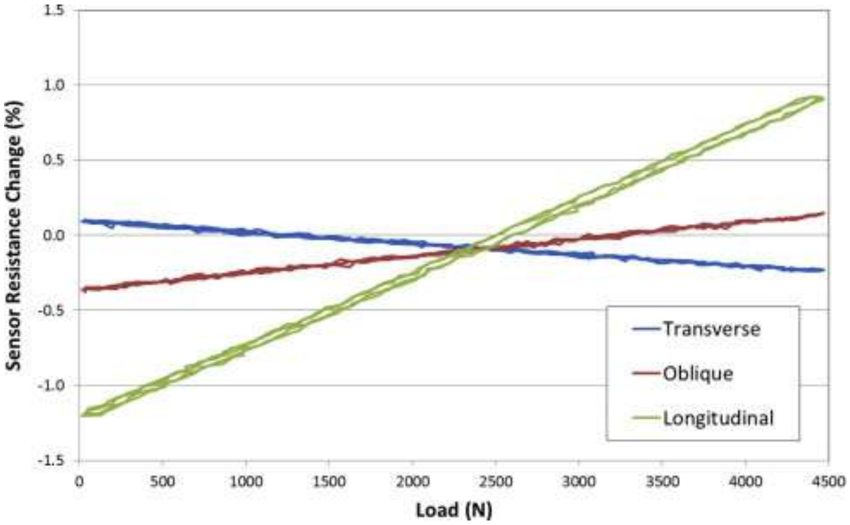


Figure 3.8 - Typical off-axis sensor response (Sebastian et al, 2014).

These results also support the idea of a complex transverse behaviour that needs further developments. Zhang et al. (2013) also test the resistivity response under cycling loading of thermoplastic polyurethane multi-walled carbon nanotubes elastomeric nanocomposite films. Samples of various filler concentrations (between 0.4% and 2.0% in mass) were prepared and loaded in a single cycle up to 30% strain. Results showed that up to a maximum of 5%, the strain-dependent resistance showed good recoverability and reproducibility after stabilisation by cycling loading. Different behaviour was observed for larger strains, where only a small part of the resistance is recoverable, which clearly reflects that the resistance is not fully recoverable after stretching. Also Ciselli et al. (2010) investigated the electrical behaviour of 0.5-5wt.% MWCNTs loaded elastomeric composites based on Ethylene-Propylene-Diene-Monomer under static and cyclic strain. It was found a linear relation between conductivity and deformations up to 10% strain, while a reversible and irreversible portion were found under cyclic deformation. The irreversible portion was attributed to damage and the reversible portion to piezoresistivity behaviour of these elastomeric composites. This important requirement for sensor materials suggests the high potential of CNTs to be incorporated into polymer matrixes for sense strain, crack and deflections.

Notwithstanding these relevant examples on the application of CNTs in PMCs to obtain the best performance from these materials, several challenges must be overcome. The properties of these nanomaterials depend on a multitude of factors. A major aspect in the study of addition of CNTs for mechanical improvement of PMCs is their dispersion in the reinforced matrix. In fact, the effective use of CNTs in nanocomposites depends on the ability to disperse CNTs within the matrix without reducing their aspect ratio. In order to overcome this problem, many mechanical/physical methods were developed in the last few years, ranging from ultrasonication to surfactant addition, from high shear mixing to melt blending and also chemical modification through functionalization and in-situ polymerization (Breuer and Sundararaj, 2004). However, further developments are still needed to effectively control and understand the dispersion process of CNTs in PMCs. Furthermore, there are other several factors that have to be taken into account: the type of CNTs used (SWCNT, MWCNT), the purity, the size (length and diameter) of the nanotubes, the interfacial adhesion between the nanotube and the polymer matrix. In fact, if the interfacial adhesion between the nanotube and the polymer matrix is not guaranteed, the nanotubes may act as “holes” in the matrix without the ability of carrying loads and transfer stresses (Moniruzzaman and Winey, 2006). If the still high cost of CNTs is also considered, there is much work to do to effectively introduce these types of materials in construction industry, especially if compared with PMCs with nanoclays. The success of these composites will depend on how effectively these challenges will be handled.

3.3 Graphene Oxide

Graphene is a two-dimensional, crystalline allotrope of carbon. In graphene, carbon atoms are packed in a regular sp2-bonded hexagonal structure, with a C-C bond length of 0.142 nm.

A graphene sheet is rolled into a cylindrical shape to form a CNT but also may be regarded as a one-atom thick layer of graphite. On the other hand, graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm. While graphite is a three-dimensional carbon based material made up of millions of layers of graphene, graphite oxide is slightly different. By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure that not only expand the layer separation, but also make the material hydrophilic. This enables the graphite oxide to be exfoliated in water using sonication, ultimately producing single or few layer graphene, known as graphene oxide (GO). The main difference between graphite oxide and GO is, thus, the number of layers. Figure 3.9 shows GO morphology in various dimensions: natural graphite at macroscale (a), 1 µm (b) and 500 nm (c) magnification SEM images obtained from a fracture surface of composite samples of 0.48 vol.% GO in polystyrene. While graphite oxide is a multilayer system, in a GO dispersion a few layers flakes and monolayer flakes can be found.

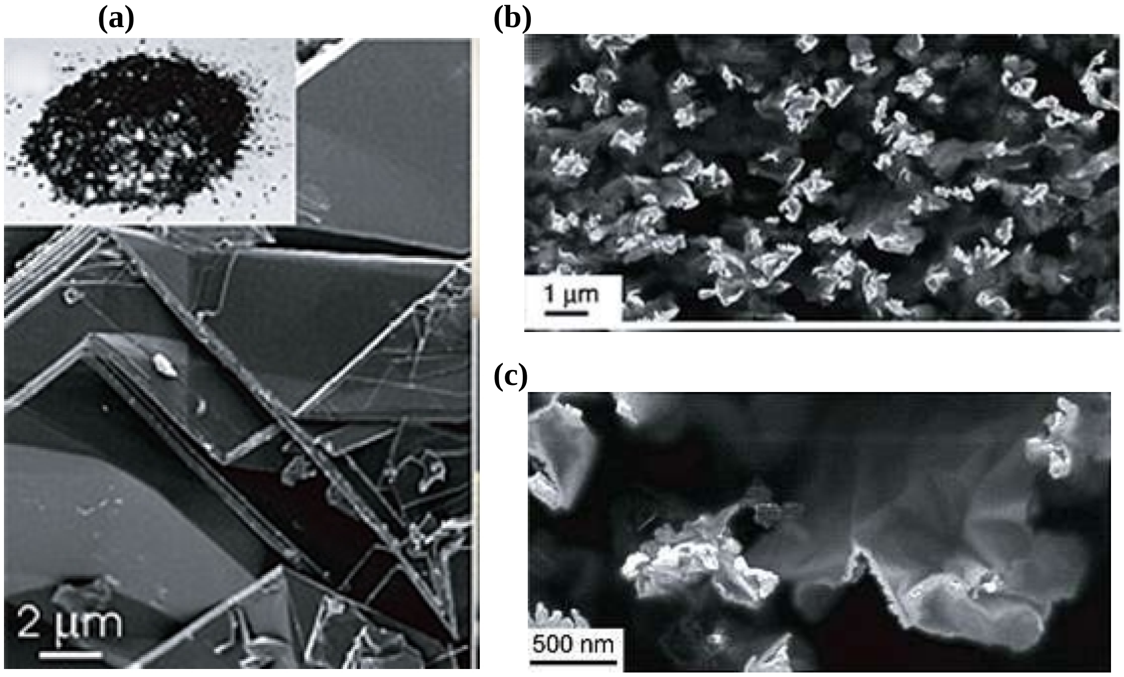


Figure 3.9 - (a) SEM and digital image (inset) of natural graphite. (b) 1 µm and (c) 500nm magnification SEM images obtained from a fracture surface of composite samples of 0.48 vol.% GO in polystyrene (adapted from Stankovich, S. et al., 2006).

Like other nanomaterials, GO has also a high theoretical specific surface area (2630 m^2/g) and high Young´s modulus (around 1 TPa), similar to that of CNTs. GO may also be viewed as a special kind of “two-dimensional fiber" (or plated fiber) for reinforcement of several types of matrices, including the polymeric one. The exceptional properties of GO nanomaterials and grapheme-based materials can possibly, beyond other applications, improve the thermal conductivity, thermal stability and dimensional stability of polymers (Dhand et al., 2013; Ma et al., 2014). However the geometry of graphite and graphene filler can also cause significant anisotropy in the thermal conductivity of the polymer composite, with the measured in-plane thermal conductivity as much as ten times higher than the cross-plane conductivity. Nevertheless, in what PMCs is concerned, GO may be advantageous in comparison with CNTs and nanoclay additives because lower nanofiller loading fractions are needed to obtain similar improvements. For example, Rafiee et al. (2010) reported the fracture toughness, fracture energy and fatigue properties of an epoxy polymer reinforced with various weight fraction of functionalized graphene sheets. Results showed that 0.125 wt% of functionalized graphene sheets was observed to increase the fracture toughness of the unfilled epoxy be 65% and the fracture energy by 115%.This can be explained by the enhanced specific area, two-dimensional geometry and strong nanofiller-matrix adhesion of GO compared to CNTs. Also several studies were performed to test other properties of graphene PMCs, namely the Young modulus and tensile strength. For example, Ma et al. (2014) investigated the structure-property relationship between an epoxy polymer and graphene nanocomposite. Figure 3.10 shows the results obtained for Young modulus and tensile strength. In fact, for an optimum value of 0.98 vol% of graphene addition a 14.1% improvement in Young´s modulus was recorded. Contrarily, a reduction of 16.4% in tensile strength was observed for a 0.984 vol% of GO nanocomposites.

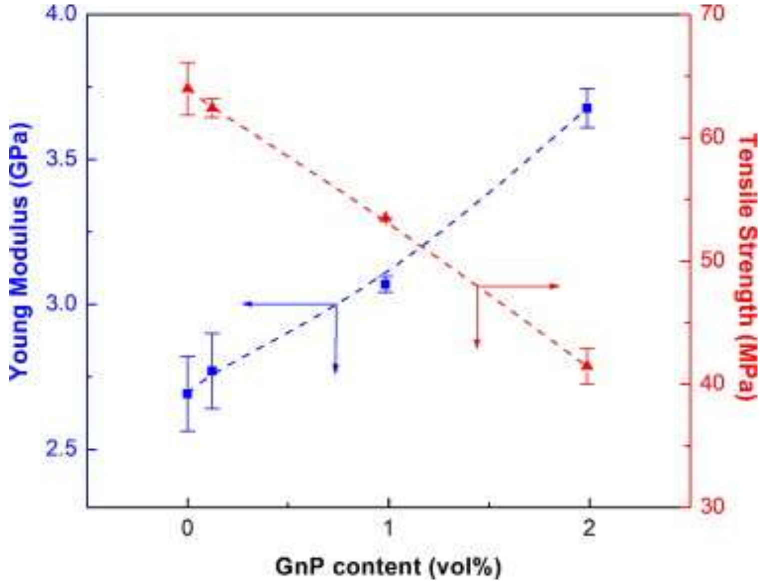


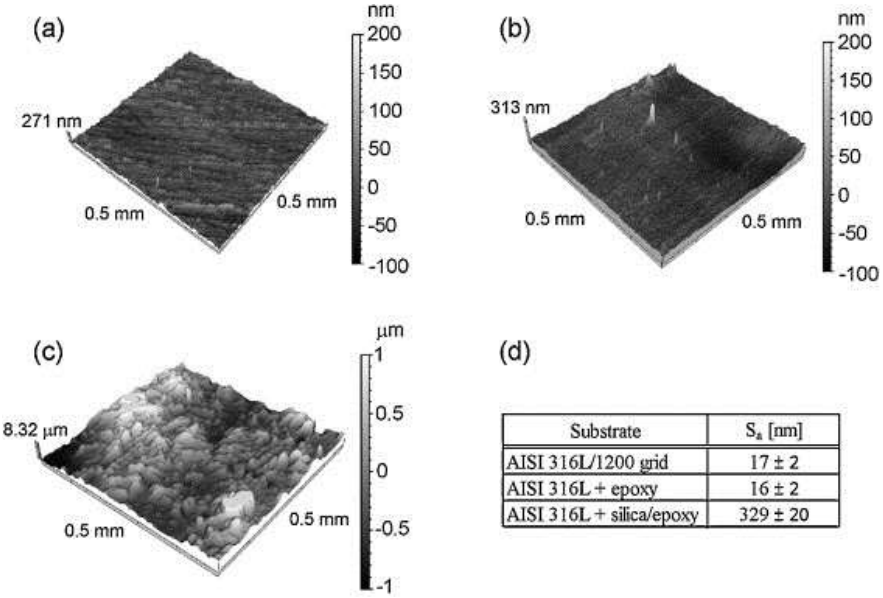
Figure 3.10 - Mechanical properties of epoxy/GO nanocomposites (Ma et al., 2014).

Although the advantages of GO seem to be great, the number of works on its application in the construction industry is small. If the addition in PMCs is considered, the number of studies is even lower. However it is possible to present some that may lead to further developments. For example, Babak et al. (2014) synthesized GO using exfoliation of graphite oxide prepared by a colloidal suspension route of polycarboxylate superplasticizer. They used it to fabricate GO-cement nanocomposites by means of an ultrasonic method and concluded that the use of an optimal percentage (1.5wt%) of GO nanoplatelets caused a 48% increase in the tensile strength of the cement mortar specimens. These authors revealed that, using FE-SEM observation of the fracture surface of the samples containing 1.5wt% of GO, these authors revealed that the GO nanoplatelets were well dispersed and no GO agglomerates were seen in the matrix. Kim et al. (2010) also suggested that graphene/polymer nanocomposites can be used in foams and other flame-retardant materials. In fact, improved thermal stability of host polymer is another benefit expected from graphene-based reinforcement. The decomposition of graphene PMCs is substantially slower than that of neat polymers, which is attributed to restricted chain mobility of polymers near the graphene surface. This means that, during combustion, inflammable anisotropic NPs form a jammed network of char layers that retards the movement of decomposition products.

For these reasons, PMCs with GO have great potential of being introduced in the construction industry in the following years. However, some barriers may slow down this move: the first one is the cost. Graphite is relatively affordable and is abundantly available around the globe and it is the only chief source for the production of graphene and graphene-derived nanofillers. However, processing graphene from graphite is an expensive process and, more importantly, there are still difficulties in handling the processes which explains why its use is not higher. Finally, more tests are needed with different polymer matrices and enhanced dispersion of graphene sheets need to be obtained to fully realize the potential of graphene-based composite materials in the construction industry.

3.5 Nanosilica

Regarding the large scope of nanotechnology, nanosilica (NS) or silicon dioxide (SiO_2) and its powderform named as silica fume (SF) have attracted considerable attention from the scientific and technical communities. As in the case of nanoclay, their remarkable properties in addition with acceptable costs justify this high interest. In fact, NS and SF have currently an important application in the production of concrete, with outstanding improvements on its properties: increased final density; reduced porosity and permeability; increased compressive and flexural strengths and decreased weight of cement used in the mix (Berra et al., 2012; Jo et al., 2007; Quercia and Brouwers, 2010; Rashad, 2014). The increased pozzolanic activity promoted by these NPs, due to their higher surface area, are contributing factors to the improvement in their mechanical properties (Chong et al., 2012). The ability of NS in filling the remaining voids in the young and partially hydrated cement paste explains the improvements in physical properties (density, porosity or workability). In terms of PMCs with NS, the possibilities of taking advantage of the NS and SF properties are slightly different. Much of the work that has been performed with NS in PMCs is related with modifying filler adhesives, reinforcement of polymeric films, and introduction in coatings production. In fact, SF is extensively used as an agent to reinforce and modify the rheological properties of liquids, adhesives and elastomers (Kessler and Goertzen, 2009). The main properties investigated include improvement in scratch and abrasion resistance, enhancing the thermal and insulation properties, as well as increasing the resistance against UV radiation (Ou and Shiu, 2010; Wang et al., 2002, 2006). Several thermosetting polymers have used NS and SF to increase their overall performance. Particular attention has been given to epoxy resins (Allahverdi et al., 2012; Chen et al., 2008; Liang and Pearson, 2009; Zamanian et al., 2013) due to their superior chemical and corrosion resistance, good adhesion and curability at ambient temperature compared to other polymers. However, epoxy resins suffer from lower thermal and weathering stability in addition to poor mechanical properties, limited coating times, and unsuitable cutting and welding properties (Bakhshandeh et al., 2014). Moreover, they also show poor resistance to the initiation and propagation of cracks. NS and SF may help to overcome some of these issues. Besides epoxy resins, polyurethanes that are widely used for sound and thermal insulation in foams have also been modified with these type of NPs (Javni et al., 2002; Lee et al., 2012; Torró-Palau et al., 2001). Polyesters should also be considered (Abd-El Messieh and Rozik, 2011). Taking into account the meaningful work that has been done, some examples are presented next on the application of NS and SF in PMCs with emphasis on the building and construction environment. Regarding the application of coatings, Conradi et al. (2014) tested epoxy coatings containing 2 wt% of 130-nm silica particles to apply in steel surfaces. The surface and morphology and mechanical properties of these coatings were compared to those of epoxy coatings without addition of NS and their corrosion resistance was also evaluated. The addition of NS significantly changed the morphology of the steel surface. Figure 3.11 shows a significant increase in the roughness of the epoxy coating with embedded NS. This change is so pronounced that it plays an important role in the coating's anticorrosion properties. An increase of approximately 40% in hardness and 5% in fracture toughness was registered. Moreover, the addition of NS induced hydrophobicity working as a successful barrier in a chloride-ion-rich environment and enhancing anticorrosive performance.



Substrate	S_a [nm]
AISI 316L/1200 grid	17 ± 2
AISI 316L + epoxy	16 ± 2
AISI 316L + silica/epoxy	329 ± 20

Figure 3.11 - Surface topography of AISI 316L surface (a) ground with Sic emery paper down to 1200 gri, (b) covered with 50 µm epoxy coating, (c) covered with 50 µm silica/epoxy coating and (d) average surface roughness, Sa, for all three surfaces under investigation (Conradi et al., 2014).

Ghanbari and Attar (2014) studied the anticorrosion performance of a clear epoxy coating with the incorporation of modified nano-silica into the polymer matrix. Different coatings with incorporation of SiO_2 contents ranging from 2-8 wt% were tested. As Figure 3.12 shows the incorporation of 4-6 wt% SiO_2 NPs possessed the best corrosion performance.

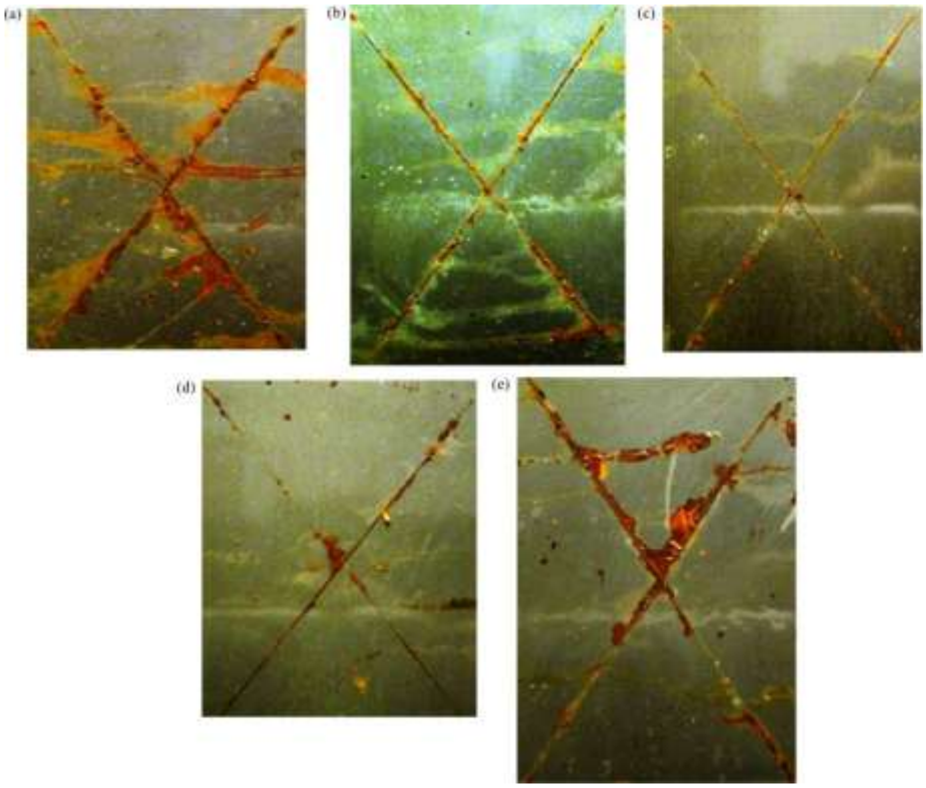


Figure 3.12 - Surface appearance of the epoxy coated specimens with different silica nanoparticle contents after salt spray testing for 200 h: (a) without nanoparticles; (b) 2 wt% nano SiO2; (c) 4 wt% nano SiO2; (d) 6 wt% nano SiO_2 and (e) 8 wt% nano SiO_2.

Also Shi et al. (2009) tested homogeneous epoxy coatings containing SiO_2, Zn, Fe_2O_3 and halloysite clay NPs applied on steel substrates. An addition of 1 wt% of NS was used. As Figure 3.13 shows, a remarkable increase of the Young´s modulus of epoxy coating from approximately 300 MPa to 2500 MPa with these NPs was obtained, much more than that obtained with other NPs. This is explained by a high improvement in the microstructure of the coating matrix. Also the corrosion rate of epoxy-coated steel was reduced by 638-2365 times with the addition of these NPs, enhancing the coating barrier performance. Allahverdi et al. (2012) used high specific surface area NS as reinforcement filler to prepare an epoxy-based nanocomposite coating. Contents of 1 wt%, 3 wt% and 5 wt% of NS were used. With an optimum value of resin filled with 5% NS, there was an increase of 26% and 21% in hardness and elastic modulus, respectively.

From another perspective, NS and SF may play an important role in polymeric foams, increasing thermal, sound and mechanical performance. For example, Javni et al. (2002) tested two series of rigid and flexible polyurethane foams with micro-silica and nano-silica. The concentration of fillers varied from 0% to 20%. NS increased the density of both types of foams only at concentrations above 20%. Above 10%, NS also lowered the compressive strength and hardness of both types of foams, but increased rebound resilience. Nikje et al. (2009) investigated the positive effects of adding NS to heat insulation polyurethane foam. Thermal and mechanical properties of polyurethane rigid foam were investigated. Up to a 2.5 wt% addition of NS, the elasticity modulus increased 28% and the temperature at 50% decomposition increased approximately 10%. However, a decrease of 20% in elongation at breakage was reported.

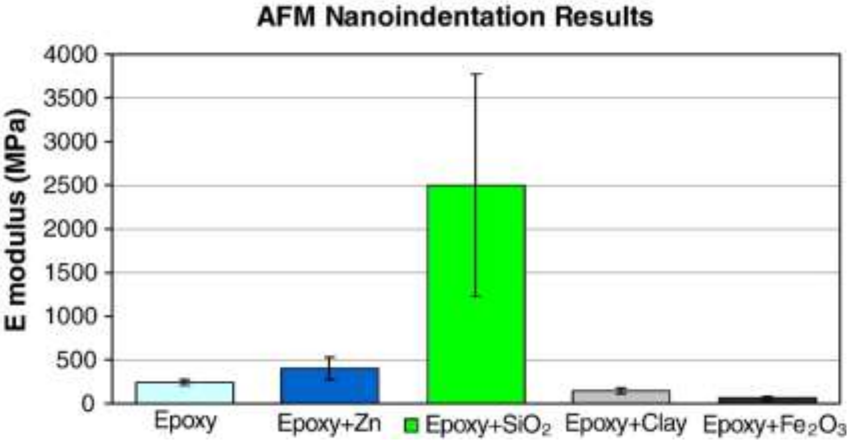


Figure 3.13 - Young´s modulus of epoxy coatings doped with different NPs. For each sample, the data were averaged from nanoindentation curves randomly selected from 256 curves obtained (Shi et al., 2009).

Adhesives should be also considered in the application of NS in PMCs. For example, Meng et al. (2014) investigated the use of NS to improve fracture toughness of polymer adhesives, focusing on the particle size, matrix ductility and adhesive thickness. Results revealed that the performance of NS as a toughening additive highly depends on the matrix´s ductility and adhesive thickness. However, in this study with merely 2.1 vol% of NS, the fracture toughness of the epoxy improved 605%.

Finally, the introduction of NS in polymer-concrete production should be considered as a valuable option. Regarding this, Pourjavadi et al. (2013) studied applications of superabsorbent polymers in cement-based materials with addition of colloidal NS. A copolymer based on acrylic acid - acrylamide was used and levels of 0.0 wt%, 0.5 wt% and 1.0 wt% of NS was added. As proposed, the addition of NS accelerated calcium carbonate formation thanks to high pozzolanic activity. Also the compressive strength increased approximately 40% for an optimum content of 1.0 wt% addition.

All these examples strongly support the statement that NS has high potential to be added in PMCs systems. However, some challenges should be better controlled. The most important is, as for other nanomaterials, the level of dispersion of NS achieved in polymer matrixes. Pristine silica is inherently a hydrophilic material that has dispersion difficulty. In this sense it is important to include coupling agents to modify the silica surface and to chemically link to silica and provide reactive functional groups (Nikje et al., 2009; Zamani Ketek Lahijania et al., 2014).

Still, if these processes are controlled, the possibilities of using NS in the construction industry are high.

3.6 Nano-Titanium Dioxide

If compared to the other nanomaterials previously referred, the application of nano TiO_2 in PMCs is undoubtedly more seldom referred in the literature. However, these NPs bring with them a different important property that justifies its inclusion in this review. In fact, thanks to their structure, TiO_2 NPs may have high photocatalytic activity, which results on (i) an environmental pollution remediation, (ii) self-cleaning and self-disinfection, (iii) high stability and (iv) relatively low cost for the materials where they are included (Agrios and Pichat, 2005; Chen et al., 2012; Hashimoto et al., 2005). For these reasons, the range of application is, for these reasons, relatively large, with the application in concrete production already in swift development (Sanchez and Sobolev, 2010). In terms of PMCs, there are lesser possibilities; however, TiO_2 NPs may be part of polymer-concrete and mainly coatings production. Among all TiO_2 NPs properties, its pigmentary properties remain the most important. Titanium dioxide is the most important white pigment used in the polymer industry, thanks to its ability to efficiently scatter visible light, imparting whiteness, brightness and opacity when incorporated into a plastic product. Moreover, TiO_2 NPs are chemically inert and insoluble in polymers. The main advantage on the use of these NPs would be to introduce “self-cleaning” and “depolluting” features in different materials (e.g. coatings and plastics) without decreasing their mechanical and physical properties.

Regarding the introduction of TiO_2 NPs in the polymer concrete production, the number of studies and results are meaningless. However, its application in coatings has been the reason for several works that have been presented in recent years and are summarized next. Pinho and Mosquera (2013) designed an innovative synthesis route for producing TiO_2 and SiO_2 photocatalysts coatings for application in stones and other building materials. The route consisted of mixing silica oligomer, Titania particles and a surfactant. It was found that increasing the Titania loading up to an optimal content of 4% an improvement in photocatalytic activity could be registered. However, this activity decreased for a higher content of 10%. Revel et al. (2013) presented some preliminary results of the EU (European Union) project Cool-Coverings that is developing an innovative polymer nanocomposite coating based on an acrylic paint and TiO_2 and Al_2O_3 NPs to be applied on different substrates. The dispersion of nanostructures TiO_2 has provided the highest increase of solar reflectance (+8.7%), while the use of Al_2O_3 as paint additive guaranteed an optimal colour matching.

Still, few references are found in the literature about the application of TiO_2 photocatalysts in building materials previously formed and produced, such as natural stone structures and existing buildings, ancient and modern. This may be justified by the very restrictive conditions of application of these products: since TiO_2 NPs are not incorporated when preparing the bulk material, it is necessary to apply to the surface of the materials as a coating. In the case of application to a major structure like a building, the requirements are even stricter because the process occurs in situ under outdoor conditions. If any additional operation is needed, such as heating or solvent extraction, the difficulties are even higher. However, the application in coatings of TiO_2 NPs in PMCs is in its first steps but the aesthetics of urban buildings and structures and the need to protect the heritage from aggressive polluted environments may justify further developments.

In order to enhance mechanical properties enhancements of construction materials, such as cement and concrete, TiO_2 NPs are less advantageous compared to other NPs like NS or nanoclay. Its addition should only be highly considered when environmental aspects are taken into account, which is more and more a reality. This could be other field where scientific research may focus.

Finally, the application of TiO_2 particles at a microscale for non-structural materials is currently a reality. DuPont Company currently provides a large range of TiO_2 products to use in construction materials production. Its application ranges from windows, deck and fencing and also home flooring products. The main advantages presented for its use include prevention of degradation of bulk materials under exposure to the sun, by absorbing the ultraviolet (UV) rays from the sun, consistence of colors and increased lifetime of the products. Although the results obtained with TiO_2 particles at a microscale are reasonable, extend the use of TiO_2 particles to a nanoscale may be other field to explore by the research community.

3.7 Concluding remarks

This chapter reviews the current research status of the field of nanoadditives in polymer matrix nanocomposites and recent key advances of their application in the construction industry. The intrinsic outstanding properties of these nanomaterials (e.g. mechanical, thermal, electrical) open opportunities in almost every technical discipline. If, in others sciences, such as medicine or the food and sports industry, these opportunities are already being exploited, the construction industry is only taking its first steps. However, with the advances in instrumentation and computational science that enable scientists and engineers to obtain unprecedented information, there is no reason to stop. Regarding this particular industry, nanoclay, carbon nanotubes and nanosilica seem to be ahead in the use in PMCs systems. Thanks to their relatively low cost production, availability and particular properties, nanoclay is still the most studied nanomaterial. The trends in the research community point towards its application in concrete reinforcement, adhesives and coatings, where the addition of nanoclay may increase, among other properties, the fire resistance. On the other hand, carbon nanotubes have impressive mechanical properties that cannot be ignored. However, the high cost of production and use of these nanostructures in PMCs prevent their massive use in the construction industry. Still, some good examples start to arise, namely in polymer concrete systems, foams and adhesives. Moreover, the opportunity of increase structural behaviour of composites materials, such as beams, by increasing the damping ratio, should be highly considered. It may be predicted that the current use of fibre reinforced polymers (FRP) to provide dynamic solutions, namely for bridges, may have further developments with the use of this type of nanomaterials.

On the other hand, nanosilica and SF already have an important role in concrete production that can justify its use in concrete modified with polymers. Its relatively low cost can also lead to further developments.

Finally, when environmental pollution remediation, self-cleaning and self-disinfection issues become important, titanium dioxide NPs are definitely the nanomaterials with more advantages. The examples of their use are still few, but their application in coatings for heritage and current buildings protection seems to be the most predictable route. Notwithstanding all this current exciting expectations, there are still some important challenges to be overcome. The most important one, common to all nanomaterials, is controlling their dispersion in the polymeric matrix. If good dispersion is not guaranteed, some of the advantages that nanomaterials have may be lost. Thus, further research results and experimental procedures are needed in order to clarify these issues.

3.8 References

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4. CERAMIC NANOCOMPOSITES

Keeping the focus on the application of nanotechnology in nanocomposites, this chapter reviews recent developments on ceramic matrix nanocomposites (CMCs). As described in Chapter One, CMCs have been less researched than polymer matrix composites (PMCs), but there has been a recent increasing interest on this type of composites. Monolithic ceramics have attractive properties like high stiffness, strength and stability at high temperatures, making them potentially useful for electronic, automotive, industrial, defence and space applications. In construction, ceramic products like floor, wall and roofing tiles, cement or bricks are major parts of a multi-billion dollar industry. However, monolithic ceramics tend to be brittle, mechanically unreliable and poor electrical conductors, which limited their use until the development of ceramic matrix composites, and now with the introduction of nanotechnology. CMCs can be extremely valuable for application with demanding thermal and mechanical requirements. CMCs open the possibility of achieving damage tolerant quasi-ductile fracture behaviour, maintaining all the other advantages of monolithic ceramics at high temperatures.

There are many different types of ceramic matrix composites. The classification is usually done according to the matrix and fibre materials, separated by a slash. For example, C/SiC is a ceramic matrix composite made of carbon fibres and a silicon carbide matrix. Besides these types of matrices and fibres materials, the classification usually separates ceramic matrix composites in oxide and non-oxide composites. Table 4.1 shows the main materials used as ceramic matrix composites according to that classification. As shown in the examples, usually oxide fibres are combined with oxide matrices and non-oxide fibres with non-oxide matrices. Thus, the main CMC types are C/C, C/SiC, SiC/SiC and Ox/Ox, where Ox represents one of the oxide materials presented below.

Table 4.1 - Main CMCs reported in the scientific community, according to the type of the matrix and fibres used.

Ceramic Matrix Composites		*Materials*	*References*
Matrix	**Non-Oxide**	Silicon Carbide	(Nozawa et al. 2009; Yu et al. 2009)
		Carbon	(Shi et al. 2014)
	Oxide	Alumina	(Zhang et al. 2008; Zhang et al. 2009)
		Zirconia	(Hannink et al. 2000)
		Mullite	(Tu et al. 1996)
		Alumino-Silicates	(Schmücker et al. 2000)
Fibres	**Non-Oxide**	Carbon	(Westwood et al. 1996)
		Silicon Carbide	(McDanels 1985; Laine and Babonneau 1993; Su et al. 2009)
		Alumina	(Tu et al. 1996)
		Mullite	(Chawla, Xu, and Ha 1996)
		Zirconia	(Vasylkiv et al. 2003)

When nanotechnology was introduced in the production of ceramic matrix composites and the analysis went from micro to nanoscale (composites to nanocomposites), some of previously existent materials lost strength and others arose. For example, the introduction of CNTs (Sarkar and Das 2014; Tapasztó et al. 2014) and graphene nanosheets (Kun et al. 2012; Porwal et al. 2013) in CMCs led to great interest of the research community due to the outstanding inherent mechanical, thermal and electrical properties of these materials. Authors reported remarkable improvements in properties like hardness, toughness, strength, damping and thermal conductivity over monolithic ceramics by using these types of fillers. For example, in the case of alumina CMCs, Fan et al. (2006) reported an improvement of approximately 100% in fracture toughness and 20% in flexural strength with the addition of only 1 wt% SWCNTs. Moreover, Walker et al. (2011) reported an increase of approximately 235% (from ~2.8 to ~6.6 MPa) at ~1.5% graphene platelets volume fraction. This chapter reviews the main developments in CMCs. As in the previous chapters, the focus of the review is on the type of fibres used. According to authors' knowledge the most important fibres manipulated at nanoscale are:

- Silica Carbide (SiC);
- Zirconia;
- Carbon Nanotubes (SWCNTs and MWCNTs);
- Graphene.

4.1 Silica Carbide

Silicon carbide (SiC) is one of the most promising structural materials due to its superior thermo-mechanical properties, such as high chemical and thermal stability, good chemical inertness, high thermal conductivity, high hardness, low density and low coefficient of thermal expansion (Zhao et al. 2014). Silicon carbide is a compound of silicon and carbon with chemical formula SiC. It occurs in nature as mineral moissanite. Because of the rarity of natural moissanite, most silicon carbide is synthetic. SiC is part of a family of materials that exhibit a one-dimensional polymorphism called polytypism. Thanks to its structure, an almost infinite number of SiC polytypes are possible, and more than 200 have already been discovered (Casady and Johnson 1996). With the introduction of nanotechnology and manipulation at nanoscale, new opportunities have been opened. One-dimensional (1D) nanostructures such as nanowires or nanotubes have gained much interest in fundamental research as well as tremendous potential applications. Among many materials, SiC based 1D nanostructures have very interesting physical, chemical and electronic properties. SiC is a wide band gap semiconductor - from 2.2 eV to 3.4 eV depending on the polytype with a high electronic mobility and thermal conductivity. One of the other merits of SiC is that it can be used at high temperatures. It is well acceptedthat its maximal operating temperature is considered to be 1200K (Latu-Romain and Ollivier 2014). Moreover, SiC is resistant to corrosive environments because of its chemical inertness. These facts justify the high application of SiC in a wide range of areas, such as electronics, heating elements and structural materials. More particularly, SiC NPs have been introduced in CMCs to enhance the mechanical and thermal properties of ceramic materials such as Al_2O_3 and mullite. It is the purpose now to present some examples of the main improvements achieved with these nanoadditions in ceramic materials and to evaluate how these improvements can be introduced in ceramic products used in construction industry.

In terms of thermal behaviour and electrical conductivity, Parchovianský et al. (2014) studied the influence of SiC NPs additions on the electrical and thermal conductivity of Al_2O_3/SiC micro/nanocomposites under normal and high temperatures. Different samples with various volume fraction of SiC ranging from 3 vol% to 20 vol% were prepared by hot pressing at 1740 ºC and at 30 MPa pressure in an argon atmosphere. The results showed that the thermal properties (thermal diffusivity and thermal conductivity) of Al_2O_3/SiC nanocomposites were not influenced by the size and shape of SiC particles, but with the volume content of these particles. Thermal conductivity increased with higher contents of SiC NPs up to a maximum of 35% increase (from 28 W/m K to 38 W/m K) for 20 vol% of these NPs. Barea et al. (2003) obtained similar trends for these properties. However, if compared with the theoretical values of thermal conductivity reported for SiC (700 W/m K) or the value measured for a polycrystalline hot pressed SiC (270 W/m K), the resulting thermal conductivity of a composite with 20 vol% of SiC should be much higher. Hasselman and Johnson (1987) stated that the existence of a thermal barrier resulted from unperfected thermal contacts at the matrix/dispersion interfaces, partially explained by the difference of thermal expansion coefficients of the two phases. Still, a relevant increase was achieved with the inclusion of SiC NPs. Regarding electrical conductivity, Parchovianský et al. (2014) also showed that the electrical conductivity increased with higher amounts of SiC NPs, especially in the composites with the volume fraction of SiC higher, or equal to 10 vol%. The results indicated that at low SiC contents the SiC particles were not interconnected to form a continuous conductive network which was verified for amounts higher than 10%, when an increase from 10^{-5} S/m (for 5 vol%) to 10^{-3} S/m (for 10 vol%) was recorded. Other studies testified identical trends, such as those of Sawaguchi et al. (1991) or Stauffer and Aharony (1992), that, based on mathematical models, proposed a value of 17 vol% of addition of a secondary phase to create an effective conductive path.

Regarding the mechanical properties of SiC ceramic nanocomposites, Zhao et al. (2014) investigated processing and mechanical behaviour of SiC - aluminium oxynitride (AlON) nanocomposites. AlON is widely used as ceramic material due to its high stiffness, good chemical stability and superior corrosion and wear resistances. However, its low flexural strength and poor fracture toughness justify the introduction of nanoadditions in the production of these types of CMCs. In this study, four samples were tested with 0 wt%, 4 wt%, 8 wt% and 12 wt% contents of SiC. The results showed interesting indicators. Concerning microstructure and density, the authors reported a decrease in the number of visible pores with the addition of SiC up a maximum reduction for 8 wt% SiC sample. For 12 wt%, an increase in the number of pores was observed, in accordance with similar works such as Dong et al. (2009), where a decrease in relative density was registered for higher contents of SiC (more than 10 wt%). Complementarily, a similar trend was observed for open-porosity and relative porosity as shown in Figure 4.1. Figure 4.1 shows that open porosity decreased with increasing content of SiC NPs up to 8 wt% and then increased with additional SiC up to 12 wt%. Accordingly, the relative density showed an opposite trend. The authors proposed some explanations for these facts, namely the agglomeration of SiC nano-particles in these composites for higher addition amounts. Moreover, Djenkal et al. (2000) also reported that additional amounts of SiC would bring a sintering inhibiting effect on the ceramic matrix, due to the strong covalent nature of Si-C bond, which makes it harder to fabricate self-bonded SiC ceramics below 2100 ºC (Bai et al. 2014).

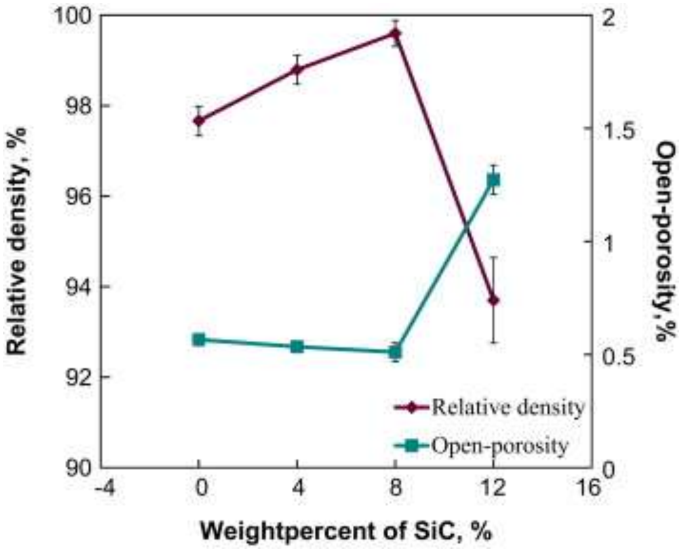

Figure 4.1 - Open-porosity and relative density of SiC–AlON composites measured via the Archimedes principle *versus* amount of SiC particles (Zhao et al. 2014).

Regarding the mechanical properties, the microhardness and Young´s modulus of SiC-AlON composites were also evaluated. Figure 4.2a and Figure 4.2b show that both microhardness and Young´s modulus increased with increasing addition of SiC NPs up to 8 wt% and then significantly decreased for 12wt%, showing a direct relationship between mechanical properties and microstructure (density) of SiC-AlON nanocomposites. Moreover, Smirnov and Bartolomé (2014) also reported that the presence of porosity generally has a negative influence on the mechanical properties, due to the concentration of stress in pores, resulting in lower strength. In addition, the authors registered similar results for flexural strength and fracture toughness. The flexural and fracture toughness were 35% and 24% higher in comparison to pure AlON for an optimum content of 8 wt% addition.

From these results, two main ideas should be empathized from the use of SiC NPs: (i) almost all properties of monolithic ceramics are enhanced, such as the thermal, mechanical and electrical properties as well as the microstructure, but an optimum value of 8-10 wt% SiC is proposed to maximize the increase in mechanical properties; (ii) the thermal properties of ceramics with SiC particles improved with increasing SiC addition content.

According to the specific functions intended for these types of materials, a reasonable value (not higher than 10-15 wt%) should be considered, in order to reconcile these two realities (optimization of strength vs. maximization of thermal conductivity). Contrarily to other nanomaterials, the dispersion of these SiC NPs into cement matrix does not seem to be a critical issue for the scientific community, justifying the high application of SiC in ceramics materials. For example, CoorsTek company (2014) develops ceramic products with the application of SiC powders. The producers present, as key benefits and properties of SiC ceramics, their high thermal conductivity, low thermal expansion coefficient, extreme hardness and chemical attack resistance, making of SiC a nanomaterial with high potential for reinforced ceramics materials.

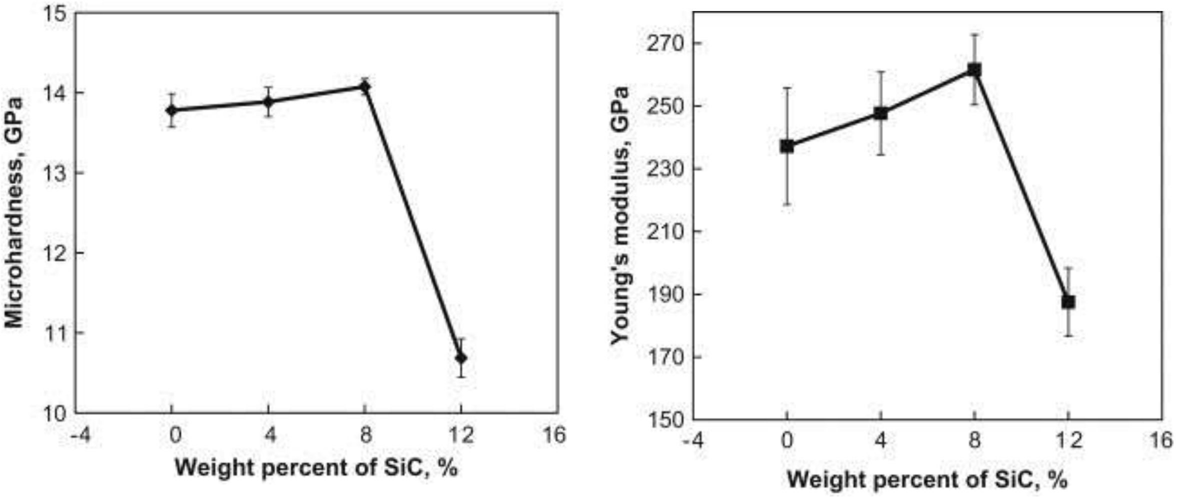

Figure 4.2 - (a) Microhardness and (b) Young´s modulus as a function of the content of SiC particles in SiC-AlON composites (Zhao et al. 2014).

4.2 Zirconia

Like SiC, Zirconia (ZrO_2) is a specific material with high potential to be used in ceramic materials, due to its high ionic and thermal conductivity, in addition to mechanical properties. ZrO_2 is a white crystalline oxide of zirconium. It can occur naturally or synthesized in three main phases: monoclinic, tetragonal and cubic. In addition, zirconia is chemically unreactive. Under higher temperatures, ZrO_2 adopts a tetragonal and cubic structure. ZrO_2 particles are used as one of the most common fillers, leading to an increase in fracture toughness and chemical inertness. Recent studies suggest that the mechanical properties of CMCs with ZrO_2 could be considerably increased by reducing the level of grain size and by achieving high levels of dispersion of these particles in the matrix. Zirconia and alumina are very often associated (Benavente et al. 2014). Zirconia Toughened Alumina (ZTA) ceramics offer an improved performance for an exceptional cost ratio. ZTA nanocomposites are attractive structural materials that combine the high hardness and Young´s modulus of the alumina matrix with an additional toughening effect of the zirconia dispersion. ZTA's are produced to contain 2-20 vol% of fine zirconia particles in an alumina matrix, with increased strength and toughness. For example, Chinelatto et al. (2014) studied the effect of sintering curves on the microstructure of alumina-zirconia CMCs. The purpose of sintering advanced composites is to control the material´s final microstructure with high densification with low grain growth and elimination of porosity. Different samples with 5 vol% of nanometric ZrO_2 inclusions in an alumina matrix were tested. The results showed an important influence of the temperature on the grain size and growth. It was observed an increase of approximately 2.5 times (from 1000 nm to 2500 nm) in the mean grain size with two distinct sintering procedures: 1500^oC and 1600^oC, respectively. These results have important consequences on the mechanical properties of CMCs that are summarized next. Most studies focus the toughening mechanisms in CMCs. For example, Benavente et al. (2014) registered an increase from 5 MPa $m^{1/2}$ to approximately 6 MPa $m^{1/2}$ in the fracture toughness for samples with 15 vol% ZrO_2 in alumina matrix for a sintering temperature of 1200 ºC and 1400 ºC, respectively. Complementarily, as Figure 4.3 shows, a significant increase in hardness and Young´s modulus was registered (from 9 GPa to 20 GPa and from 300GPa to 367 GPa, respectively) for samples with 10 vol% of ZrO_2.

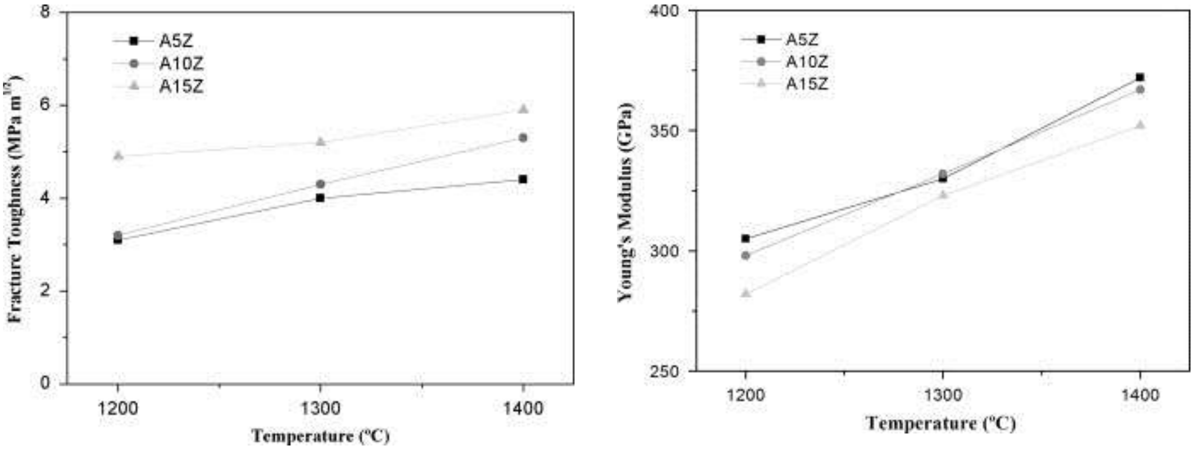

Figure 4.3 – Influence of microwave sintering temperature on : (a) fracture toughness and (b) Young´s modulus of Al2O3-ZrO2 materials with different contents (Benavente et al., 2014).

Zirconia can also be used as the matrix and alumina as the addition. For example, Vasylkiv et al. (2003) produced zirconia ceramic with 1 wt% to 5 wt% Al_2O_3 addition. The authors obtained an average hardness and toughness for 2.5 wt% alumina addition of 16.23 GPa and 7.86 MPa m$^{1/2}$, respectively.

Zirconia can also play an important role as a ceramic matrix material. Danilenko et al. (2013) studied the effect of nickel oxide (NiO) in ZrO_2 composites. The authors registered that NiO and inclusions can increase the indentation fracture toughness of zirconia-nickel oxide composite material more than 50%, but only when the sintering occurs in a neutral atmosphere.

In this context, CoorsTek Company (2014a) also developed zirconia ceramic products named Technox® zirconia (2014) for application in several industries, such as refractories, telecommunications or electronics with the following advantages: high strength, high fracture toughness, high wear resistance, good frictional behaviour, low thermal conductivity and electrical insulation. Still, as observed for silicon carbide, if improved electrical properties are needed, other nanomaterials are more suitable, such as carbon nanotubes or graphene oxide.

4.3 Carbon Nanotubes

The excellent properties of CNTs together with their one-dimensional nature (high aspect ratio) dimensionality make them ideal candidates for reinforcement in almost any type of materials. CMCs are naturally included in these areas, where CNTs can be used as toughening elements to overcome the intrinsic brittleness of the ceramic materials. Thanks to their structure, CNTs tend to form complex networks of aggregates within composite materials, playing a major role in defining the mechanical, electrical and thermal properties of the composites (Cho et al., 2009). The majority of works addressing CNT composites was focused on polymer matrices, whilst comparatively few investigations explored inorganic (ceramic) matrices and the potential of CNTs reinforcements as toughening mechanisms. However, the increasing interest on CNTs applications and fabrication with less expensive cost maintain the potential of this issue. For example, Cho et al. (2009) presented an extended overview on CMCs containing CNTs. According to the authors, for successful CNT/composite development, two major challenges must be considered. Primarily, CNTs with intrinsically good mechanical properties must be obtained in reasonable quantity at acceptable cost for consistent introduction in materials production industry. Secondly, CNTs must be processed in such a way that a homogeneous dispersion is obtained within the matrix with an appropriate degree of interfacial bonding.

These requirements are naturally common to all CNT composites, but in the case of inorganic matrix composites, such as ceramics, they play a key role in the production of CMCs with CNTs. In the case of CMCs, obtaining a high degree of inorganic matrix densification without damaging the CNTs is a widely discussed and challenging task. A good dispersion of CNTs in composites means that that the individual nanotubes are distributed uniformly throughout the matrix and well-separated from each other. However, CMCs with CNTs tend to form aggregates spontaneously during the growth process. These agglomerates are extremely undesirable especially in ceramic matrices, as they may act as defects leading to stress concentration and premature failure. Figure 4.4 shows the typical microstructures of agglomerated (Figure 4.4a) and homogeneous (Figure 4.4b) CNT/glass matrix composites. CNTs easily agglomerate thanks to their high aspect ratios and typically poor interaction with solvents or cement matrix composites. Within CNTs, SWCNTs are more prone to agglomerate into “ropes” or “bundles”, consisting of many parallel nanotubes bound by Van der Walls forces. These agglomerations lead to a decrease in mechanical and functional properties of CMCs.

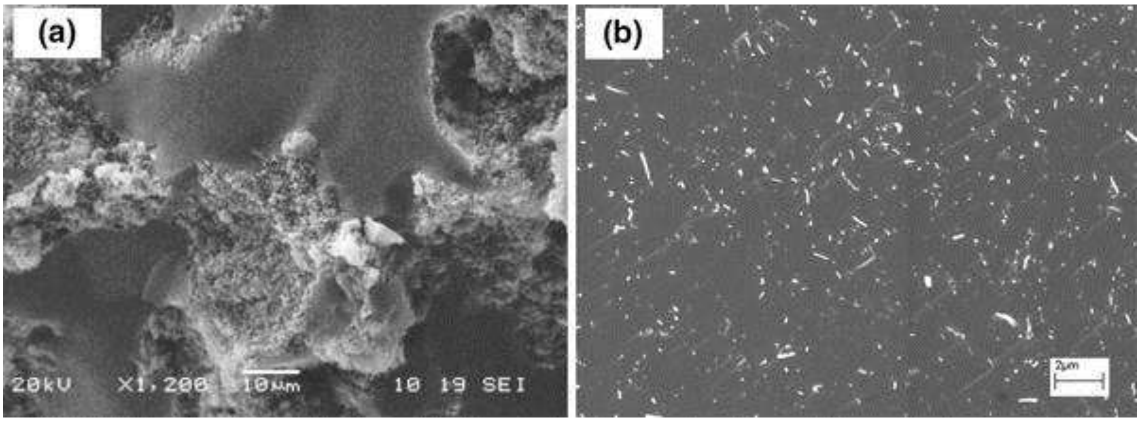

Figure 4.4 - SEM images of fracture surfaces of (a) agglomerated CNTs in a borosilicate glass matrix and (b) homogeneously dispersed CNTs in a silica matrix (individually pull-out CNT segments can be observed that may be related to possible toughening mechanisms)(Cho et al., 2009).

Typically, high loading fractions favour agglomeration, because particles come into contact more often, which explains common results for CMCs where properties are enhanced at low loading fractions but cannot be increased further due to CNT agglomeration above a small vol%. In fact, with good dispersion, each CNT is loaded individually over a maximum interfacial area, contributing directly to mechanical and toughening mechanisms. However, the situation becomes more ambiguous when addressing transport properties, such as electrical conductivity, as a network of touching CNTs is desired. Also in this case, the results indicate that an initial good dispersion favours these properties, allowing the network to form by itself. To overcome the problem of dispersion of CNTs issues many different approaches have been proposed ranging from ultrasonic action, functionalization of surfaces and use of surfactants (Fedosova et al. 2014; Hilding et al. 2003). In terms of CMCs, colloidal processing, sol-gel processing and electrophoretic deposition gain advantage as potential techniques to assure a good dispersion of CNTs in ceramic matrices.

Notwithstanding these dispersion issues, CMCs with addition of CNTs still attract much attention from the research community, due to potential significant improvements on mechanical and functional properties. Thanks to the brittle property of ceramic materials, most of studies aim to increase the fracture toughness. However, improvements extend to many other properties, such as flexural and bending strength, compressive strength, Young´s modulus and electrical properties. Estili and Kawasaki (2008) developed an approach to mass-producing CNTs alumina composites with optimized and controlled compositions. Authors stated that homogeneous composites can only be obtained for CNT concentrations in the range of 2.4-16 vol%. However, an increase of 70% in the fracture toughness from 3.12 x 10^6 Pa $m^{1/2}$ for monolithic to 5.20 x 10^6 Pa $m^{1/2}$ was registered only for alumina composites with 3.5 vol% of CNTs. Also Jiang et al. (2007) produced 10 vol% SWCNTs-Al_2O_3 composites by the spark plasma sintering (SPS) method that exhibit excellent toughness, ranging from 6.9 x 10^6 Pa $m^{1/2}$ (221%) to 9.7 x 10^6 Pa $m^{1/2}$ (310% increase related to monolithic alumina composite). Regarding fracture toughness, similar results were presented by other authors (Zhan et al. 2003; Fan et al. 2006). Despite these positive results, the alumina composites with CNTs addition have not been sufficiently documented and recently some contrasting results came up. For example, Aguilar-Elguézabal and Bocanegra-Bernal (2014) studied the fracture behaviour of alumina ceramic reinforced with a mixture of 0.05 wt% MWCNTs + 0.05 wt% SWCNTs. Although the small amounts of CNTs added to the alumina matrix, the results showed a general decrease in Vickers hardness and fracture toughness for these samples compared to monolithic alumina matrix (Figure 4.5). The hardness and fracture toughness of the CMCs with different types of CNTs were much lower than those of pure Al_2O_3 (17.05 GPa and 3.34 x 10^6 Pa $m^{1/2}$, respectively). The lowest hardness and fracture toughness values were registered for the composites reinforced with the mixture of SWCNTs and MWCNTs (12.45 GPa and 1.96 x 10^6 Pa $m^{1/2}$, respectively), due to the higher porosity and the presence of clusters or bundles of CNTs that undoubtedly act as defects with no load carrying ability.

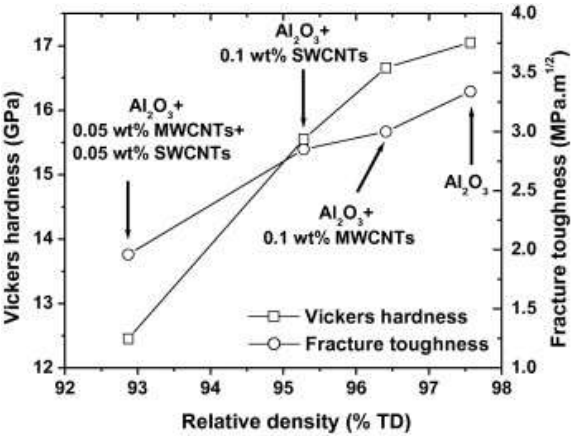

Figure 4.5 - Variation of Vickers hardness and fracture toughness with relative density for various nanocomposites (Aguilar-Elguézabal and Bocanegra-Bernal 2014).

Also Gallardo-López et al. (2014) tested the effects of SWCNTs on the hardness and flexural strength of alumina matrix composites. Samples of fully dense Al_2O_3 and SWCNTs composites with 1, 2, 5 and 10 vol% of SWCNTs were fabricated by colloidal processing and tested. The results showed neither increase nor decrease of hardness for samples with 1 vol% SWCNTs with respect to monolithic alumina. Moreover, a 25% decrease in hardness was found for composites with higher SWCNTs content (3, 5 and 10 vol%). Similar trends were found for flexural strength where a significant decrease was found for samples with higher contents of SWCNTs addition (48.7% decrease for 2 vol%).

These contradicting results show that much has to be done to determine ideal experimental conditions and materials processing to obtain consistent results in the addition of CNTs in ceramic matrices. From the literature, authors put forward for reflection the following aspects:

- Mechanical properties are strongly affected by grain size. The CNT refinement effect on the matrix grains is greater at higher temperatures (1550-1600 ºC) (Gallardo-López et al. 2014). Recently, Hanzel et al. (2014) developed a new approach based on the functionalization of MWCNTs by acid treatment, and stabilization of alumina/MWCNT dispersion at high temperatures (1550 ºC) with subsequent freezing. Figure 4.6 shows the high levels of dispersion obtained for the samples tested in this study.

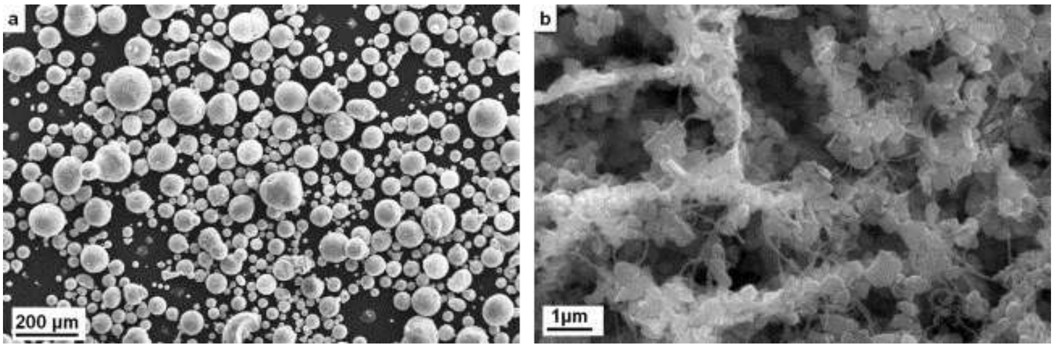

Figure 4.6 - SEM images of (a) granulated alumina/CNT composite powder and (b) detail of granulate surface with distribution of MWCNTs and alumina grains (Hanzel et al., 2014)

- Many authors (Zhan et al. 2003; Wang 2004) questioned the validity of the method used to measure fracture toughness using micro-hardness method based on the following equation:

  $$K_{IC} = \alpha\left(\frac{E}{H}\right)^{1/2}.\left(\frac{P}{C^{3/2}}\right), \quad (1)$$

  where E and H are Young´s modulus and hardness, respectively, P is the applied load, c is the radial crack length and α is an empirical constant which depends on the geometry of the indenter. Authors argue that the validity of the fracture toughness results depends critically on the elastic/inelastic contact-mechanical response of the material under test.

These issues should be considered and studied to fully take advantage of CNTs potentialities in ceramic products. Despite these important aspects, CNTs have also been tested to increase the electrical properties and structural health monitoring capabilities of CMCs. For example, Inam et al. (2014) developed a novel method for analysing structural health of alumina nanocomposites filled with graphene nanoplatelets CNTs and carbon black nano-particles. A change in electrical conductivity was analysed after indentation to understand the structural damage and try to establish some kind of correlation. The results showed that the change in electrical conductivity is highly dependent on the type of filler and number of indentations or damage. Damage was indicated by an irreversible decrease in electrical conductivity for the indented nanocomposite bars.

Moreover, despite the massive advantage of the use of alumina as ceramic matrix in the literature, due to its high resistance to corrosion, chemical stability and hardness, other ceramic matrices were used. For example, SiO_2 matrices were used with different contents of CNTs additions and the results showed similar trends to those obtained with alumina (Andrade et al. 2008; Zheng et al. 2008). Still, the attention of current research is mainly aimed at achieving good dispersion of CNTs in all of these types of cement matrices.

4.4 Graphene

Graphene (GO) has gained increasing interest from the research community in almost all areas. However, probably due to problems with the dispersion of CNTs in CMCs, studies involving the incorporation of graphene in ceramic matrices have highly increased in the last few years. Graphene with its combination of a large specific surface area, two-dimensional high aspect ratio sheet geometry and increased mechanical properties shows great potential as nanofiller in composite materials. In chapter 3 the application of graphene in polymer matrices was reviewed, representing the majority of works made with this nanomaterial. However, the improvements on mechanical and thermal properties in PMCs have opened new perspectives for its use in bulk ceramics. The first reports on graphene/alumina composites occurred in 2009 (He et al. 2009), where 5% of carbon was added to the alumina matrix via milling alumina and graphite in ethanol at room temperature. Since then, much has been done. Records of improvements involve mainly properties like fracture toughness, electrical conductivity or Vickers hardness. For example, Centeno et al. (2013) prepared GO/Al_2O_3 powders and tested their mechanical and electrical properties. Regardless of the well-known problems of aggregation when reduced oxide is directly used as the second phase in hydrophilic matrices, the resulting slurries of GO/Al_2O_3 showed very good dispersion. As a consequence, the authors registered good impacts in both electrical and mechanical properties. As Figure 4.7 shows an increase of 50-80% in fracture strength compared to monolithic Al_2O_3 was registered. For an optimum value of 0.22 wt% GO addition, an increase of approximately 80% was observed. Moreover, Vickers hardness of the composites was very similar to the one of the monolithic alumina. This means a good dispersion of the graphene phase that avoids the deterioration of this important property (Figure 4.8).

Wang et al. (2011) developed another example of a graphene/alumina CMC. GO nanoplatelets were added to an Al_2O_3/water dispersion. Among several improvements, the authors registered an increase of approximately 53% of the fracture toughness compared to that of pure alumina. Moreover, an increase of the electrical conductivity up to 172 S m^{-1} was achieved. Also Chen et al. (2014) added GO nanosheets to alumina composites by hot pressing in contents ranging from 0.1 to 1.0 wt%. These additions had impact in almost all properties of the resulting samples. Primarily, a decrease of approximately 20% (from 2.51 μm to 2.0 μm) in average grain size was observed when GO was added to alumina matrix. The introduction of GO nanosheets hinders the growth of alumina particles making much finer particles resulting in more homogeneous materials as shown in Figure 4.9 (He et al. 2009). Figure 4.9a shows large and uneven grains for the monolithic alumina. Contrarily, GO composites exhibit a remarkable decrease in the grain size (Figure 4.9b).

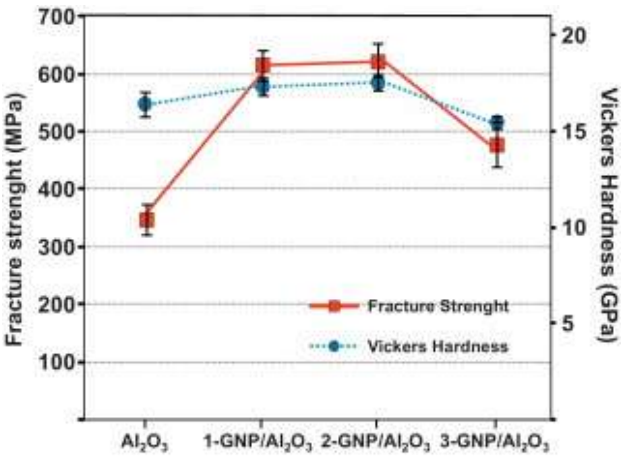

Figure 4.7 - Mechanical properties of the composites and the alumina (Centeno et al. 2013).

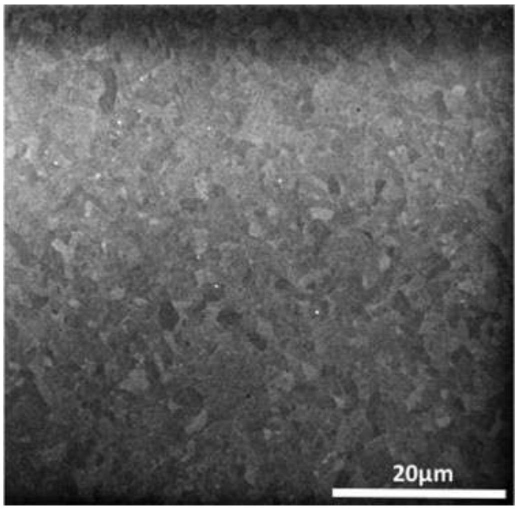

Figure 4.8 - SEM image of 0.22 wt% GO/ Al2O3 polished surface (Centeno et al. 2013).

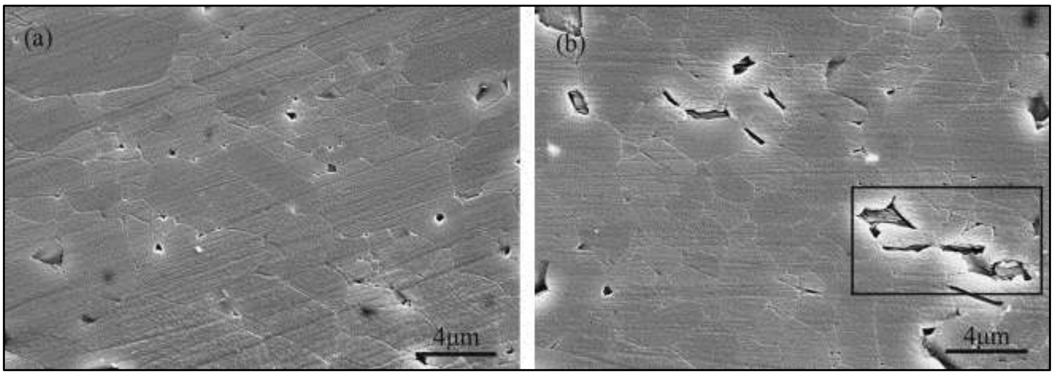

Figure 4.9 - Mechanical properties of the composites and the alumina (Chen et al. 2014).

Consequently, the authors registered an increase of approximately 43.5% of the fracture toughness for an optimum value of 0.2 wt% of GO/alumina composite. Also the bending strength increased by 28% (from 420 MPa to 540 MPa) with GO addition for an optimum value 0.1 wt%. Moreover, GO addition has high impacts on cracks propagation. The authors registered four different toughening mechanisms: crack deflection, enhanced by the large specific surface area of GO nanosheets (Figure 4.10a); crack stopping when cracking slows down or even stops by the action of graphene nanosheet (Figure 4.10b); crack bridging when GO nanosheets effectively dissipate fracture energy (Figure 4.10c); crack branching which constitutes cracks in lengths of several micrometres, which contributes to the increase of toughness (Figure 4.10d). Similar phenomena were reported by several other authors (Kim et al. 2014; Walker et al. 2011; Centeno et al. 2013; Porwal et al. 2013).

Although the great majority of works regard the application of GO in alumina matrices, these outstanding results extend to other types of matrices. For example, Hvizdoš et al. (2013) tested a series of silicon nitride based CMCs containing 1 and 3 wt% of four types of graphene platelets. The results showed that graphene does not tend to extensive clustering, only occasional stacks are observed. This is in fact a great advantage of GO addition in ceramic matrices, especially when compared to the application of CNTs. Moreover, the introduction of GO leads to better wear resistance. A decrease of 60% was registered in samples with 3 wt% addition of graphene nanosheets. Also Walker et al. (2011) registered a remarkable 235% improvement in fracture toughness due to the addition of only 1.5 vol% of graphene in silicon nitride.

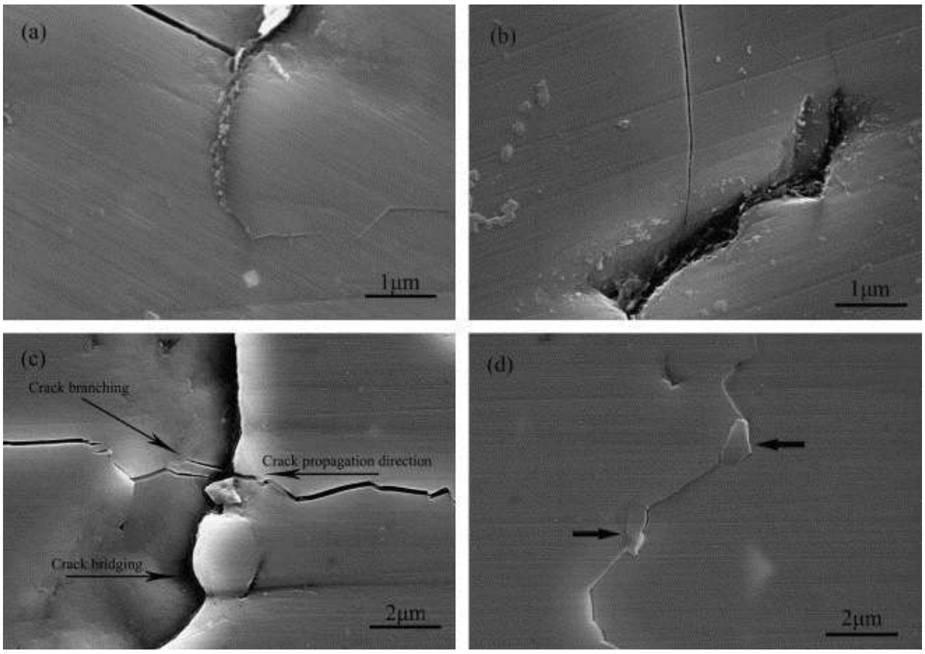

Figure 4.10 - FESEM images of Vickers indentation fractured surfaces indicating the toughening mechanisms: crack deflection (a); crack stopping (b), crack bridging (c) and crack branching (d) (Chen et al. 2014).

Although the number of publications of GO ceramics nanocomposites is relatively limited when compared to other nanomaterials, such as Silicon Carbide or CNTs, there are no claims of a decrease in mechanical and functional properties of these nanomaterials. In fact, the potential of using these NPs is so high that some authors are recently patenting processes and methods to produce these composite materials. For example, Corral et al. (2013) patented novel graphene-reinforced ceramic composites and methods for making such composites materials with small amounts of these nanomaterials (0.02 to 1.5 vol%). The perspectives of using GO in CMCs production for high temperatures applications justified their efforts to publish and protect such methods.

4.5 Concluding remarks

This chapter reviewed the current research status of the field of ceramic nanocomposites (CMCs) and recent developments in this area. The range of application of CMCs compared to polymer nanocomposites (PMCs) is considerably smaller, especially within the construction industry. Ceramics usually play a non-structural role in construction, with the main applications ranging from floor, wall and roofing tiles to bricks or glass. For example, ceramic tiles are used for floors, walls and similar materials are used to furnish bathrooms. These ceramic products are durable, relatively hygienic and normally used to add aesthetical value. Additionally, for these types of applications, ceramic products show high stiffness and strength, good corrosion resistance and low thermal and electrical conductivity. The introduction of nanotechnology has allowed increasing all these properties. Moreover, with nanotechnology new features can be added to ceramic products. For example, the introduction of CNTs or graphene allowed some ceramics to exhibit high thermal conductivity and/or high electrical conductivity.

In terms of thermal behaviour, fracture toughness and chemical resistance, silicon carbide, zirconia and alumina show more consistent results. Their incorporation in ceramic matrix has as primary impact an improvement of the microstructural composition with high densification, low grain growth and elimination of porosity. Consequently, it impacts other properties. For example, silica carbide shows potential to increase the thermal behaviour up to a maximum of 35% for a 20 vol% addition. For additions under 20 vol%, both silica carbide and zirconia additions increase the fracture toughness up to 35% and 50-100%, respectively. Additionally to these improvements, the dispersion of these nanopowders in ceramic matrices is currently relatively controlled, justifying the investment of some manufacturers in producing these nanopowders, such as CoorsTek (2014).

Still, the biggest potential of development of hi-tech ceramic materials is the opportunity of adding carbon derived nanomaterials, particularly CNTs and graphene. Regarding CNTs, their incorporation has a tremendous impact on almost all properties of ceramic materials. For example, the results showed up to 310% increase in fracture toughness for 10 vol% addition of SWCNTs. Also the electrical conductivity can increase up to 45% with the addition of CNTs for 5-15 vol% addition. However, the dispersion of CNTs in ceramic matrices represents a critical issue that has been preventing further developments. CNTs tend to form agglomerations, particularly in cement matrices, acting as defects leading to stress concentration and premature failure. The techniques used to process CMCs with CNTs have gradually provided better and more consistent properties compared to traditional powder processing methods. However, further developments are still required to develop higher quality samples in sufficient quantities to provide reliable results.

The problems related with the addition of CNTs enabled graphene to gain preference in the application in CMCs. The results indicate similar improvements in mechanical properties to those of CNTs, such as improvements up to 235% in fracture toughness for only 1.5 vol% addition. The authors focused much attention on describing the toughening mechanisms with the addition with these types of NPs. Also the electrical conductivity increased up to 172 S m-1. Despite these positive results, more research is needed in order to define optimal contents and processing methods to consistently achieve these improvements.

If these issues become increasingly more controlled and the impact in other mechanical properties (such as compressive strength, bending strength) becomes accurately estimated, it is possible to expect that ceramic materials can be introduced as a structural material in the near future. For example, Kaneko and Li (1992) have already introduced in early 90´s a feasibility study of structural systems (beams, composite beams and structural joints) made from ceramics. Since then, the discovery and the emergence of new high potential nanomaterials, such as CNTs in 1991 (Iijima, S. 1991) opened new possibilities that may provide further developments in this issue.

4.6 References

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5. INTEGRATED VIEW - FUTURE DEVOLOPMENTS, TRENDS AND CONCLUSIONS

This dissertation summarized the main developments observed in nanotechnology with direct impact in construction industry. The new paradigm observed in the construction industry characterized by the openness to apply new technologies in methods and processes and by new perspectives concerning the use of nanotechnology in the "next generation" of materials has justified this work. The number of research works within this issue has continuously increased in the last decades with proved advantages of the addition of NMs. The key to the implementation of nanotechnology in the market is to clearly present the specific advantages, risks and implications that NMs and related products may have in the construction industry. This was the main objective of this work.

In this sense, three main sub-areas of the construction industry were discussed: cementitious materials (cement and concrete), polymers nanocomposites and ceramics nanocomposites. Concerning each of these topics, the work was structured according to the NMs that may have impact on the properties and performance of the materials in order to understand the characteristics and the potential of each nanomaterial as well as presenting known applications in construction industry.

5.1 Advantages of nanomaterials for structural applications - Conclusions

Table 5.1.1 and Table 5.1.2 summarize the main conclusions of the whole work in terms of the top 5 NMs with higher impact and potential. It presents the main advantages in each subject and the direct application known for construction industry. In general terms, it may be concluded that currently the greatest impact to the construction industry market is likely to come from enhancement of performance of materials. For example, the addition of nanomaterials in the concrete production may have great impacts in terms of the mechanical properties, namely compressive and flexural strength. Moreover the increase of the anticorrosive performance (barrier in chloride-ion-rich environments) may impact the durability of concrete and its structural behaviour during its life cycle. On the other hand, the use of nanomaterials to produce adhesives and epoxy resins with increased mechanical properties opens the opportunity to further developments in reinforcing concrete and steel structures, namely bridges with different types of joints. From other point of view, it is expected that, in the medium to long term, nanotechnology development will lead to truly revolutionary approaches to design and produce brand new materials and structures with much improved energy efficiency and adaptability. For that it is predicted that nanotechnology must follow the same long path that FRPs have been doing in the last decades with great impact on the market of construction. Regarding nanomaterials, Table 5.1.1 and Table 5.1.2 also show NMs with different potentialities and various ranges of applications. The ones that stand out the most are:

- Nanosilica (SiO_2) - Great potential to be used in cement and concrete production when high strength is needed. Also great impact on C-S-H production, hydration rate, microstructure among other important properties of concrete. Within nanotechnology in concrete production, this is the nanomaterial with more consistent results. Furthermore, it may be used in other structural applications, such as the use of polymeric coatings with anticorrosive properties in harsh environments, namely in steel bridges;

- Nanotitanium Dioxide (TiO_2) - Great potential to be used when environmental pollution remediation, self-cleaning and self-disinfection features are relevant. Its photocatalytic property may be of use in almost every construction material, where coatings are advantageous. These types of coatings may be applied in a wide range of surfaces, such as concrete (pavements and roads), glass and polymers substrates. Its application may reduce NO_x levels up to 80%. The example of "Dives in Misericórdia" church and TiO_2 based coatings from Dupont Company (2015) to be applied in almost every type of surface are good examples of the advantages of using TiO_2 NPs;
- Nanoclay - It has as its main advantage the relatively low cost and ease of production. Although nanoclay does not have the potentialities of other NMs it is possible to achieve consistent improvement in materials properties, particularly in concrete and in the production of coatings. In the first case, the addition of nanoclay leads to a denser and more stable structure of concrete with impact on its mechanical properties (e.g. compressive strength). In terms of coatings, the addition of nanoclay creates a barrier to water vapour penetration as well as a reduction of chloride content (up to 69%) in the case of application of concrete, leading to an effective way of protection of concrete under harsh environments;
- Carbon nanotubes (CNTs) - They have impressive mechanical and electrical properties that can play an important role in almost every area of construction. For example, its application in concrete and cement production may lead to great improvements in mechanical properties, namely Young´s modulus (up to 50%) and flexural strength (25%), failure strain and toughness. For that, it is necessary to guarantee an appropriate dispersion of CNTs in the mixes, which cannot be always ensured. In fact, this is one of the main issues to be dealt with in order to take full advantage of these type of nanomaterials, complementarily to its high costs. On the other hand, CNTs also have high potential to create sensors than can be incorporated in different materials, such as concrete or polymers, giving the materials the ability to detect cracking and failure. Compared to other materials, the tremendous mechanical and electrical properties allow these improvements with very small contents of addition, mainly under 1.5-2.0 wt%. The main challenges on the wider use of CNTs remains on its price and the ability to uniformly disperse CNTs in the matrices, mainly in polymer and ceramic matrices;
- Graphene oxide - Its potentialities are comparable to those observed with CNTs. They may allow impressive improvements in concrete and cement mechanical properties (e.g. up to 50% in flexural strength and up to 33% in compressive strength), with low contents of addition (under 2.0 wt%). Furthermore graphene oxide shows high potential of increasing the properties of ceramic matrices materials, and an acceptable level of dispersion may be achieved with these NPs in the matrix. These improvements range from an increase of up to 80% in fracture strength with 0.25 wt% addition to an improvement of up to 235% in fracture toughness with an addition up to 1.5 vol%. The main drawback of the use of these NPs is its high cost of production and to ensure high levels of dispersion of these nanomaterials in the matrices, similarly to CNTs.

Table 5.1.1 **-** Summary of the most relevant NPs and its impact on different construction materials properties (adapted from different sources)

Nanoparticles (NPs)	Construction materials	% addition	Investigated properties - (%) indicates property improvement compared to monolithic	Products
Nanosilica (SiO_2)	Cement and concrete	0.0-10.0 wt%	- Compressive and flexural strength of concrete (up to 75%) - Density and microstructure - more uniform, denser and compact products - Hydration peak temperature (13%) - Reaction rate (30%) - Thermal behaviour - compressive strength of 28 days under high temperatures (400 ºC) (70%) - Abrasion resistance (100-180%)	Cuore concrete
	Polymeric coatings			
	Steel (epoxy matrix)	0.0-3.0 wt%	- Hardness (up to 40%) - Fracture toughness (5%) - Enhanced anticorrosive performance - barrier in a chloride-ion-rich environment- corrosion rate 638-2365 lower - Coating Young's modulus - from 300 MPa to 2500 MPa - Elastic modulus (up to 21%)	
	Polymeric foams			
	Polyurethane	0.0-5.0 wt%	- Elastic modulus (up to 28%) - Thermal behaviour - temperature 10% higher at 50% decomposition - Elongation at rupture (20% lower)	
	Adhesives (epoxy)	0.0-5.0 wt%	- Fracture toughness (up to 605%)	
	Polymer concrete	0.0-1.0 wt%	- Accelerated CSH formation - Compressive strength (up to 40%)	
Nano-titanium dioxide (TiO_2)	Cement and concrete	0.0-20.0 wt%	- High photocatalytic activity - NO_x degradation (65-80%)	TioCem
		0.0-3.0 wt%	- Compressive strength (45%) - Increased resistance to water permeability	
		3.0-5.0 wt%	- Compressive strength - 28 days (up to 30% less) - Flexural strength - 28 days (up to 25% less) - Pore structure and density - harmless or slightly harmful pores	
	Polymeric coatings	0.0-4.0 wt%	- Improvement in photocatalytic activity - Solar reflectance (up to 9%)	DuPont Company
Nanoclay	Cement and concrete			
	Nano-metakaolin	0.0-8.0 wt%	- Compressive strength (up to 7%) - Tensile strength (up to 49%) - Promote hydration process	
	Nano-montmorillonite	0.0-1.0 wt%	- Compressive strength (up to 20%) - Permeability coefficient (up to 25% lower) - Denser and more stable structure	
	Halloysite	1.0-3.0 wt%	- Compressive strength (up to 24%) - Gas permeability (up to 56%) - Denser and more stable structure	

Table 5.1.2 - Summary of the most relevant NPs and its impact on different construction materials properties (adapted from different sources).

Nanoparticles (NPs)	Construction materials	% addition	Investigated properties - (%) indicates property improvement compared to monolithic	Products
Nanoclay	Polymer coatings			NanoCor Products
	Concrete	1.0-5.0 wt%	- Cover pores and voids - Permeability (50% less) - Chloride content (69% less) - Porosity (more than 10% less) - Barrier to water vapor penetration (30%)	
	Polymer - concrete	1.0-5.0 wt%	- Tensile modulus (up to 13%) - Ultimate tensile strength (20% lower) - Failure strain (50% lower) - Compressive strength (up to 15%) - Fracture toughness (up to 8%)	
Carbon nanotubes	Cement and concrete	0.0-0.1 wt%	- Flexural strength (up to 25%) - Young's Modulus (up to 50%) - Reinforce nanostructure - decrease nanoporosity - Increase C-S-H production	
	Sensors (concrete, polymers)	0.4-2.0 wt%	- Sense micro-cracking and failure - Strain-dependent resistance recoverability up to 10% strain	
	Polymer concrete	0.0-1.5 wt%	- Failure strain (290%) - Toughness (105%) - No impact on early age compressive strength	
	Epoxy resins	0.0-0.5 wt%	- Tensile strength (2.25 times higher) - Deformation at failure (3.27 times higher) - Damping ratio (up to 700% higher)	
	Adhesives/adhesive joints	0.1-2.0 wt%	- Normalized creep - 0.1 wt% (54% reduction) - Cracking under cyclic loads (13-20 times higher)	
	Ceramics			
	Alumina matrix	2.0-10.0 vol.%	- Fracture toughness - non-consensual results highly dependent on dispersion ranging from 27% decrease to 310% increase - Similar trends for flexural strength and hardness	
Graphene oxide	Cement and concrete	0.05-2.0 wt%	- Flexural strength of cement (up to 50%) - Compressive strength of cement (up to 33%) - Tensile strength of cement mortar (up to 48%) - General decrease in porosity	
	Polymer - epoxy resins	0.0-0.125 wt%	- Fracture toughness (up to 65%) - Fracture energy (up to 115%) - Young's modulus (up to 14%)	
	Ceramics			
	Alumina matrix	up to 0.25 wt%	- Fracture strength (up to 80%) - Vicker hardness - similar to monolithic ceramics - Bending strength (up to 28%) - High toughening mechanisms - crack stopping	
	Silicon matrix	up to 1.5vol%	- Fracture toughness (up to 235%)	

Despite all these potentialities and advantages of using NMs in construction materials, there is a lack of extensive applications of NMs in the construction industry, much more when structural applications are considered. Apart from some adhesive applications for reinforcement and the production of concrete with increased properties (e.g. Cuore Concrete), it seems that the commercial market still does not know how to introduce and take full advantage of these products.

5.2 Drawbacks and challenges

In the construction industry, the development range of products and solutions based in nanotechnology goes from concepts and ideas to products that are already commercially available. Closing the gap between laboratory achievements and the real-world suitability is the biggest challenge.

The impact of these solutions on the commercial market has been influenced mainly by a limited product awareness within the industry, the traditionalism and skepticism of the construction industry, an excessive focus on the initial investment over life-cycle cost, and the environmental impact and safety.

The most important issues that need to be overcome are:

- Cost - Construction is a cost-driven sector. The initial investment (higher than it is at the moment) remains the main obstacle to the implementation of nanoproducts, despite the long-term benefits that could be obtained from their use. In fact, the costs of most nanotechnology materials and equipment are relatively high which is due to the complexity of the equipment used for the preparation and characterization of these products. Expectations are that costs will decrease over time, as manufacturing technologies improve and demand increases. It is a challenge to the construction industry to solve production and distribution problems and to provide solutions to the general public at a reasonable cost;
- Manufacturing - Existing products are quite expensive, mostly due to the processing technologies not being convenient for large-scale production. As long as there is not enough demand, the nanoproducts will remain a “novelty” and will not take the industry to the level that is needs to be completely automated. Additionally, the lack of availability of good quality NMs in large volumes may explain why NMs are not currently used more extensively. Therefore, one of the possible paths for the future is to focus on the optimization of nanoproducts and NMs production;
- Health and environmental - The effect of various NMs on the natural environment is a subject of debate within the nanotechnology and environmental research community. Some of the potential problems on this matter include leakage of materials into groundwater, release of materials in the air through the generation of dust and exposure to potentially harmful materials during construction and maintenance operations. Therefore, there are some reasonable concerns about the potential adverse health and environmental effects related to the manipulation and use of NMs. The wide range of properties that make NMs so useful, such as their size, shape and surface characteristics, can also cause potential problems if the material is not properly used. For example, nanotechnology-based construction products may cause respiratory problems to construction workers related with the inhalation of dust and aerosols;
- Skepticism of stakeholders and consumers - The construction sector is one of the most conservative industries and it is very difficult to implement new techniques and materials. The stakeholders

and contractors are extremely reluctant to change the materials and the way they work. This is one of the reasons why the implementation of nanotechnology is so low in the construction industry, despite the increase of products commercialized and all the research that has been made in the last years. The skepticism of consumers about the benefits and properties of products containing NMs and also the concerns about safety issues are other factors which slow down their adoption by the sector. For that reason, it is important that the major companies supplying materials for the construction sector foster comprehensive marketing campaigns promoting the use of NMs while explaining the benefits of their application.

In the future, the construction industry will be compelled to embrace new technologies in order to deliver safer, more sustainable and more cost-efficient buildings and infrastructures. This will drive continued research to the development of an increasing number of suitable NMs solutions and products for the construction industry.

5.3 Future developments

Taking into account all the advantages and drawbacks presented, nanotechnology clearly has the potential to be the key to a brand new world in the field of construction and building materials. The key to development remains on the countries that decide to profit from this opportunity with investment in research and production of nanobased materials. Figure 5.1 shows that the most developed countries have realized this opportunity where the USA, Russia and Asia countries (China and South Korea) show the faster growth rates.

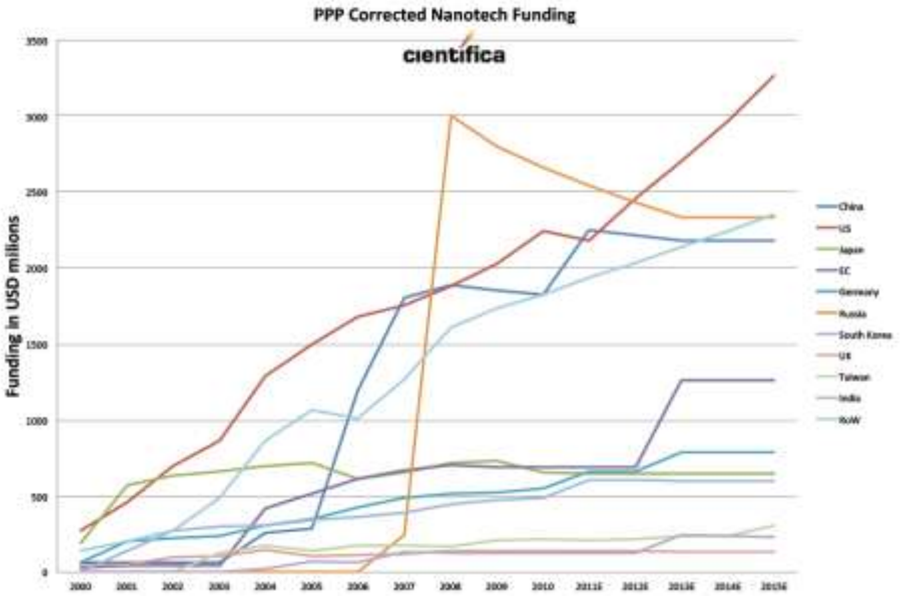

Figure 5.1 - Purchase Power Parity (PPP) corrected nanotech funding in USD millions dollars by country (Científica, 2011).

However, most of European countries, in particular Portugal, are lagging behind the main developed countries, since they started later than their neighbours to invest on nanotechnology projects. Still, Portugal is increasingly investing more sources on nanotechnology and different networks and centres have been opened in the last years. For example, the International Iberian Nanotechnology Laboratory (http://inl.int/about-inl/what-is-inl) that opened in 2005 in Braga as a result of a joint decision of the Governments of Portugal and Spain was the first fully international research organization in Europe in the field of nanoscience and nanotechnology. Its research areas are focused on four major vectors: nanomedicine; environment monitoring, security and food quality control; nanoelectronics; nanomachines & nanomanipulation. The research area of nanomaterials and the construction industry is thus not, for the moment, a focus of this organization. Based on the conclusions of this dissertation regarding the potential of nanomaterials to apply in the construction materials, Portuguese scientific research institutions, in particular the research units of IST, with focus on the new Platform for Nanotechnology and Materials (IST-NM) (https://fenix.tecnico.ulisboa.pt/investigacao/IST-NM), have the opportunity to take an important step forward in this issue, being ahead in terms of research and aligned with community "hot topics". In this sense, the issues with the most potential and value to be developed in future projects of research are:

- In the short term, the application of Nanosilica in cement and concrete production promises larger possibilities of studies addressing the mechanical behaviour of some structural elements, such as beams, columns or slabs. The method to produce concrete with improved properties with these NPs is relatively defined, allowing starting making the bridge between these studies and the mechanical behaviour of its use in structural elements;
- The most widespread applications in a few years' time is predicted to be with nanotubes, due to their outstanding mechanical properties, as stated in section 2.8. For that purpose, a better knowledge of their capabilities and processing methods is needed. To overcome current problems in bonding CNTs with different matrices, particularly the cement matrix, future investigations are needed to provide a better understanding in the areas of: CNTs content inside any possible matrix (specially their application in concrete pastes); purification methods to achieve uniform dispersion of CNTs within the OPC paste; theoretical modelling of CNT-OPC interaction. Overcoming these issues means many other researches addressing all the possibilities of applying CNTs in the construction industry: ultra-high-performance concrete; production of smart materials (with self-sensing capabilities); mechanically improved polymers nanocomposites with increased carrying loads ability;
- The area of coatings is currently the issue with more known applications in the construction industry. Although it has lower impacts on the structural behaviour of buildings, the opportunity to give structures anti-corrosion protection, self-cleaning and depolluting effects should be considered. In this sense, future technical research should be focused on the application of nanocoatings over different surfaces and testing of their behaviour under harsh environments. For example, studies about the anti-corrosion effect of a Nanosilica coating in metallic surfaces or the self-cleaning effects of TiO_2 coatings in glass or concrete would be relevant. The importance of protection of bridges and other structures subjected to harsh environments may justify all of these works;
- Nanosensors are also an interesting issue although a vast number of new publications and tests are required in order to be ready for large structural applications. CNTs and graphene oxide are the NPs with most potential to be used in these devices.

5.4 References

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