

Hybrid Nano-Composite Design for Nano-Architecture

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Abstract

The aim of this research is to create a comparison and correlation between the treatments in medicine in terms of “bone regeneration”, the treatments in architecture in terms of “nanolime consolidation effects on limestone” and the treatments of aerospace technology in terms of anti-icing nano-coatings techniques in order to prevent the effect of freeze-thaw cycles in CH buildings. The criteria to be discussed related to these issues will be the porosity and mass transport between the correlation of human bone and limestone, and anti-icing nano-coatings between the correlation of aerospace engineering techniques to adopt into preserving CH buildings against the freeze thaw cycles.

The issue will be held in 2 main steps: 1ST Step: As reference to Faculty of Medicine: France; University of Orleans (Almhdie et al., 2014) on bone regeneration therapy: Absorption of compatible nano-chemicals (nano-silica SiO₂, HAP<200nm particle size, CaO, Ca(OH)₂ nano-composite design) treatment to inner porous structure : limestone, in order to have mechanical strength and consolidation. 2ND Step : As reference to AIRBUS ICEPHOBIC Anti-icing Nano-Coatings Technology European Commission Project – Polytechnique Montreal Canada – Functional Coatings and Surface Engineering Laboratory (LaRFIS): Anti-icing icephobic nano-coatings of the porous structure (limestone) against the problem of freeze-thaw cycles and building material deterioration on cultural heritage buildings. (coatings made of silica nanoparticles).

Expected result of the 1st step nano-treatment is to gain mechanical strength and consolidation effect inside the building material, regarding as the main treatment. Then, in the 2nd step, regarding as the after treatment therapy with the anti-icing nano-coatings, the expected result will be to prevent the CH buildings against their well-known problem of freeze thaw cycles, caused by the thermal effects and the temperature differences between day and night, and summer-winter, especially in the regions where the humidity and rain factor are the basic factors for deterioration, caused the ice formation and the cracks inside the building material structure.

Research questions of this thesis; firstly, by using the techniques in medicine for “bone regeneration”; how to find a solution to the well-known two problems of the nanolime treatment in architecture ; reduced penetration and accumulation, whitened deposition. How to solve the problem of reduced penetration and accumulation in porous structures in order to increase the capability of their treatment efficiency?

How to solve the problem of whitened deposition in nanolime? Secondly, by using the techniques in aerospace technology, used by AIRBUS, for “anti-icing nano-coatings technology”; how to find a solution to the well-known problem of freeze-thaw cycles and ice-formation inside the building structure, that finally cause and effects the building material deterioration.

During the study, the discussion will be focus on the solutions for sustainability of nano-treatments in nano-architecture for future. The discussion points are; hybrid nano-composite design, “a simulation of bone regeneration in medicine”, in which ways and techniques? “HAP hydroxyapatite - SiO₂ - Ca(OH)₂” hybrid works well to solve the problem? Which hybrid nano-composite design could be the best solution? In which synthesis technique to form the hybrid nano-composites works better? Which criteria effects the

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efficiency? How to get a better penetration and consolidation in porous structures: “bone and limestone” ?
How to avoid the back migration of nano-particles?

The idea of this research has application to patent for Politecnico di Milano POLIMI IRIS: 05.1. Brevetto & Patent Application: 2018. NANOTECHNOLOGY IN ARCHITECTURAL RESTORATION: SCIENCE & INNOVATION: Hybrid Nano - Composite Design for Consolidation of the Porous Structures: Limestone & Bone “Transport Phenomena”, ID: hdl:11311/1065405

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1. Introduction

Nanotech; it sounds as a magic when it is firstly pronounced, but indeed, the term “nano” indicates only a measure, a dimension that is hardly difficult to understand with its incredible littleness. Nanosize is the first thing when it comes to understand what nano is, and 1 nm is 1.0×10^{-9} m in size. Regarding this little size, it is obvious that the issue for nanotechnology depends on highly “quantum confinement effects” (Eaglesham, 2011). To be clear to understand the link between medicine to nanotechnology, collagen fibers with the role of giving tensile strength and flexural strength inside bone structure (Fernández, 2015) is approximately 500 nm size, hydroxyapatite crystals with 50 nm size, while tropocollagen inside the collagen fiber is only 1.5 nm size. (Gao et al., 2017) For a decade, the nanoscience created innovative solutions for the bone regeneration problems in medicine. Especially the osteoporosis therapy (Almhdie et al., 2014) and the dental fracture problems (Whitbeck et al., 2011) find innovative solution techniques by using different nano components. The little size of nanotech provides inner penetration and a full effect on material morphology, that make the dreams come true in medicine. So, for this research, the issue will be discussed through the aims and questions; if it is possible to simulate these medical innovation techniques to preservation of architectural monuments, especially built with limestone, and how it is possible to make this simulation, which nanohybrids and combinations could be more suitable for this sense. Primarily, the research hold in University of Orleans in France [1] shows great correlation between limestone and bone morphology with the proof of the high resolution X-ray computed tomography images that makes obvious the similarity of these two structures in terms of “morphology, texture and topology”. This proof could be a starting point to create the idea of the new nano hybrid design in order to create more compact and more durable structures for architectural concept, not only for preservation but also for consolidation the defects with suitable formulated nano hybrids design parameters. Moreover, with a plus of after treatment, with the experience of Airbus PHOBIC2ICE European Commission Project (Klemberg-Sapieha, 2016) with LARFIS Functional Coating and Surface Engineering Laboratories in Canada, ice formation that happens above the the aircraft surfaces has been discussed to resolved by using nanoparticles with a surface treatment system that invites the architectural science researchers to find ways of prevent the freeze thaw cycles problem in cultural heritage buildings which has been known one of the major factors of deterioration, especially in the regions under pressure of the humidity factor and the temperature differences. To sum up, bu using the science and innovation of

nanotechnology, with the practice of reading the results for a decade, in a good way, the interdisciplinary solutions between medicine, architecture and aerospace technology could create new ways and findings to design new nano hybrids that will provide the next generation solutions to unresolved problems of nanotech.

2. Background

2.1. Si-HAP Reinforcement

Cambridge University study (Thian et al., 2007) indicate that silicon substituted hydroxyapatite (HAP) has managed to get successful results for medicine, even if, under 5% silica substitution in combination with HAP crystals, by the technique of the coating, using magnetron sputtering. The focus in the research based on not only hard tissue replacement therapy in medicine but also it is claimed that soft tissue replacement could be possible and effective in this sense. This medical innovation opens the idea of designing new nanohybrids that can be useful for architectural applications, in a similar way with bone regeneration with the simulation to limestone regeneration, based on the proof of the Orleans University Hospital research has been discussed above. (Almhdie et al., 2014) On the other hand, Berkeley National Laboratory and Imperial College London studies (Fu et al., 2012) has the concept of designing new nanostructured combinations in different ratios to have the desired compressive strength for bone structure. Curve simulations has been performed successfully during these research to find the optimal conditions that will suit best with the expected results and can able to solve the problems of “load bearing bone defects”. In a similar way, load bearing effects are the major problem for the pillars of the cultural heritage (CH) buildings under pressure of the huge domes or magnificent upper structures above these standing pillars. Generally, pillars in mosque or churches are the primary deteriorated part of a CH building structure for a possible earthquake effect or anything else that can cause a huge damage. Usually replacing the pillars technique has been done after these kind deterioration problem, and replacing the pillars also accompany with the question of the authenticity of these CH structures. So, meaningfully, much more suitable solution could be not to replace, to take precaution and prevent the damage. This means, it is possible to strengthen the pillars of an architectural structure by using to enhance the mechanical durability and strengthening techniques of nanotechnology. By this way, replacing the pillars will be not necessary any more, until it could be the last solution to save the rigidity of the structure. Before this step, it is sure that nano science and reinforcement techniques of nanotechnology that has been continuing to work well both in nano medicine (Fu et al., 2012) and nano engineering during a decade, could be the first and primary saving methodology in terms of the preserving the authenticity in CH monuments. Replacement a pillar, indeed, must be the last case, the last chance to save and preserve. But, unfortunately nowadays, it is a widely used method in lots of restoration works in Zeyrek region in Istanbul-Turkey. Preserving the original and providing the authenticity must be the first approach of each restoration work, as regarding with the Venice Charter. (Congress and H. Monuments, 2011) In Article 10 of Venice Charter, it is officially advised to enhance the limits to the new technology capabilities if the traditional techniques could be inadequate to succeed the expected results and the new technology has the necessary scientific data to use.

2.2. Understanding the Experience on Dental Application Techniques and How to Adopt this Success in Medicine to Architecture

Human dentin has also some similar problems in the sense of deterioration, in a basic way, such as a complication of bone defects has been shown. For this reason, researchers are trying to find solutions by using the methodology of nanoscience, with the studies has been done for the evaluation of the effectiveness of calcium hydroxide. (Whitbeck et al., 2011) These studies continue on not only for the fracture resistant on dentin but also the capability of elimination of the bacteria in root dentin by using the idea of calcium hydroxide and calcium oxide nanoparticles. (Louwakul et al., 2017) It is obviously clear in the results that nano-sized calcium hydroxide and calcium oxide have been shown great importance to eliminate the bacteria however the standard sized chemicals of the same components have no effect. In this concept particle size is the major factor for nanotech to make the applications effective and to gain the expected results. Also for the hydroxyapatite treatments, the desired particle size advised to be under the limits of 200nm particle size for the medical applications in literature, and for the nanostructured based treatments on architectural conservation works, the desired limits are advised to be between 25-50 nm size. (G. Borsoi et al., 2016) part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations.

2.3. Understanding the Effect of Particle Size on Success from Medicine to Architecture

With the brushing application techniques basically, penetrating diammonium phosphate chemical to stone based structures has been tried to searched before in the literature, without nano particle size effect on efficiency. (Sassoni et al., 2013), (Sassoni, 2018) Diammonium phosphate treatments is a common usage for cultural heritage stone conservation, and a well-known general traditional application technique that can seem relatively successful in its own limits. What makes the innovation for the nanostructured particles is the incredible littleness of their capabilities that creates the huge effect on permeability inside the inner structure of the morphology. In the research study has been completed in the University of Edinburgh (Campbell, 2013), it is obviously shown that fine particle sized hydroxyapatite (between the range of nano to fine powder size) can able to create an effect on archeological bone structure. In Edinburgh University research study, it is discussed between the correlation of the success in 3 different type of lithotypes: limestone, portland cement and archeological bone, and the discuss criteria is the transport phenomena and the particle transport effect on these different morphologic media. Hydroxyapatites has been preferred to synthesised and colloidal stability has been discussed as a research question in the second step. Results have been shown that, the success and the penetration depth of HAP are highly depends on the criteria of agglomeration that hinder the effect of good penetration. For Edinburgh University study, hydroxyapatite – ethanol suspensions can able to succeed the penetration until 6mm because of their undesired agglomerates between the spectrum of 20-600 nm size particle size hydroxyapatite colloidal suspensions, whereas 200 nm stable particle size of HAP crystals offers much more success in biomedical applications in literature for human bone systems in terms of osteoporosis treatments. (Durgalakshmi

et al., 2014) Also, hydroxyapatite crystals with different percentage of the reinforcement (20%, 40%, 60% and 80%) (Zarifah et al., 2016) in process by [SiO₂, CaO, Na₂O and P₂O₅] composition, widely known “45S5 Bioactive Glass” with the official name in the medical literature; performed good results for bone regeneration therapy in medicine, not only with combinations in hydroxyapatites but also by itself as a role of being a scaffold in bone tissue engineering applications. (Fernández et al., 2015), (Thavornnyutikarn et al., 2014), (Zarifah et al., 2016). 20-200nm particle size range spectrum also has been advised in the architecture literature with the experience on limestone applications. (PhD Dissertation, 2017) For this concept, the key point is to determine the right size range and to select the appropriate spectrum for a better penetration, by avoiding the agglomeration and to be sure with the homogeneous distribution of the substrate chemicals with the role of the stable size nanoparticles between the range to 20-200 nm particle size.

3. Methodology

3.1. Interdisciplinary Era Between Medicine to Architecture and How to Adopt the Nano-tech

For all the cases of the applications in interdisciplinary area regarding both medicine, architecture and aerospace technologies, the primary rule to understand is there are essential factors that will highly impact on the results on nanotreatment. Dealing with chemicals, even if in nano-size, is much more difficult to overcome the problems that will affect the efficiency and could be a major disturbing factor coming from the environmental conditions such as temperature and relative humidity. (Borsoi et al., 2017) Apart from this, to enhance the composition of the solvent some researches indicate that the percentage between two or more solvent component used together effects the homogeneity and distribution performance of the colloidal nanoparticles in their related solvents. (Daehne and Herm, 2013) Another clue to get the effective results is to avoid back migration criteria, the cause effect harmony is making sense for this case, as the magic comes from the littleness of the nanoparticles that creates the innovation, on the other hand, this littleness can able to cause the undesirable effect that is called the back migration of nanostructured particles. For instance, nano-titanium dioxide particles are known the disadvantage of losing from the surface by the affect of rain (Sassoni, 2018), even though the economical value of titanium dioxide application is so high to worth to mention.

On the other hand for medical applications, in terms of the bone regeneration therapy, and building the bone tissue engineering scaffolds, “silica calcium phosphate composites” find themselves application area in nano-medicine and they are widely used with the crucial factors of pore size and interconnection layers between Ca-P and Ca-Si, for their success criteria that affects the adsorption, adhesion and formation efficiency. (Ghannam, 2004) “45S5 Bioglass” scaffolds have a major impact on nano medical therapies with their capability of interconnections and reaction potential between some other basic chemicals such as SiO₂, MgO and CaO, that creates the different durability performance on compressive strength and tensile strength. (Gerhardt and Boccaccini, 2010) For bone regeneration therapy applications, some optimization of the

performance simulation graphics has been evaluated in the literature that could be accepted a proof for the connection between the porosity of the material structure between the compressive strength, under the affect of the application with different chemical composition nanohybrids such as Na_2O , CaO , SiO_2 , P_2O_5 [8], (Ching et al., 2009). In order to evaluate the porous scaffold reliability, [CaO , Al_2O_3 , P_2O_5 composition] has been used to detect the flexural strength of the load bearing capabilities [8], (Pernot et al., 2010). Meaningfully these chemical compositions has been similar for architectural researchers who has been inverstigated for the Roman Mortar composition. A study that has been performed on Berkeley Laboratories have the great importance to introduce with the science world that Roman Mortar has the potential to be a composite material, by specialising a combination of the “calcium-alumino-silicate” minerals that creates the potential of reinforcement and durability. (Prince, 2018) With all these experiences coming together in different interdisciplinary areas from medicine, bone tissue engineering to architecture, science world introduce to all researchers a truth that nano composite combinations and nanohybrids have lots of cross sectional key points that needs to be taken into account and to go deeper in consideration inside.

3.2. 5 Key Point Rule and The Optimal Efficiency List

Considering the efficiency criteria among these different disciplines, there are 5 key points that points out all the attention; penetration depth, surface adhesion, viscosity, adsorption and substrate porosity have the main impact on all disciplines performance criteria regarding the nanotech innovation. (Daehne and Herm, 2013) Apart from these, as a reference to studies that has been carried out in TU Delft, storing conditions of the nanomaterials, preparation and mixing techniques, finding the most suitable solvent to get homogeneous distribution, density of the colloidal suspension, application process, properties of the substrates or the lithotypes, pre-treatment or after treatment possibilities, environmental conditions (temperature, T and relative humidity, %RH), air velocity (that will affect the criteria of the solvent evaporation rate), techniques such as brushing, full saturation bath, spraying or nebulization in order to get the desired homogeneous distribution among the structure’s deeper side and a so crucial factor of sonication that will also affect the colloidal stability are the basics of the optimal efficiency list on nanoscience. (PhD Dissertation, 2017), (Borsoi et al., 2017), (Borsoi et al., 2016), (Borsoi et al., 2012).

3.3. Hybrid Nanocomposite Design from Nano-medicine to Nano-architecture

The recent research works that has been carried out especially in Horizon projects focused on creating new design nano-composites with combination of some well known nano- particles such as nanostructured titanium and zirconium particles. (Gherardi et al., 2018) Titanium composites in nanosized has been widely used for the stone preservation cases in architectural heritage science thanks to its self cleaning potency. (Russa et al., 2016), (Bergamonti et al., 2013), (Crupi et al., 2018). Also in some studies for preservation again, antibacterial affect of titanium has been discussed. (Russa et al., 2014)

Apart from titanium, Ca(OH)_2 such as known as nanolimes has been evaluated in lots of research studies, and some of them with good results. (Dissertation, 2017), (Daehne and Herm, 2013). Although, effective results has been announced in medical treatments using the HAP hydroxyapatite particles, by using the advantage of the 70% composition similarity depends on the mineralogical part of bone composition (Thavornytikarn et al., 2014), a study that has been published in Nature Journal announced that Ca based designed nano-hybrids such as CaSi ceramics (with their official literature names: diopside and akermanite) has better potential effect on bending strength than HAP based treatments, regarding the medical treatments on bone with stem cell therapy. (Gao et al., 2017)

Ca based hybrids, in combination with carbon nanotubes (CNT) has been firstly discussed in the literature, as a master thesis study that has been carried out in ITU Istanbul Technical University, between 2013 to 2016 and has managed to get 5 times mechanical strength enhancement effect on limestone structures. (Sungur, 2016) During the work, the analysis has been performed under the financial support of research funding TUBITAK, Turkish National Research Council and finally has gained the scientific innovation patent with the patent number 2017/17231, the results regarding as follows:

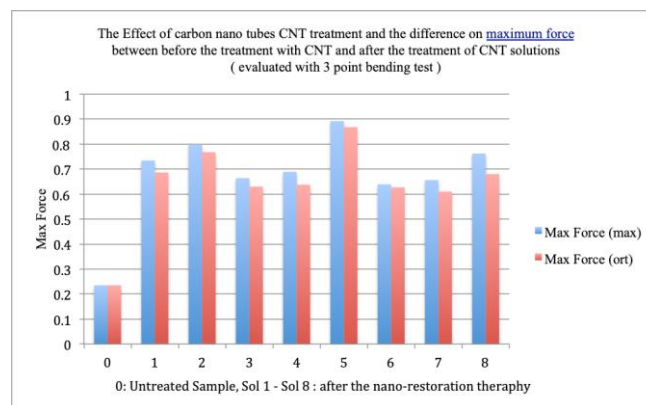


Figure 1: The difference between Max Force (average) and Max Force (max). The effect of nano-restoration treatment on tensile breaking force. (Sungur, 2016)

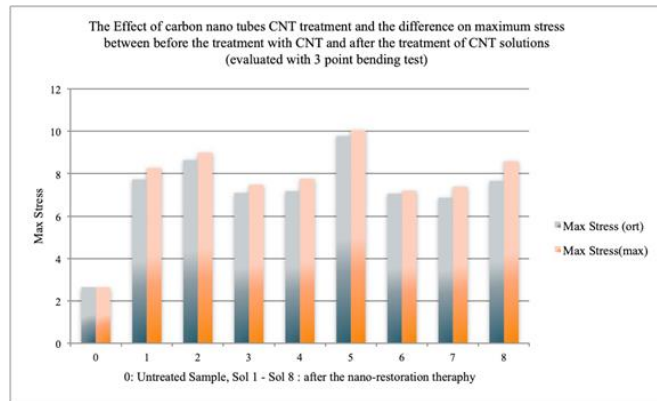


Figure 2: The difference between Max Stress (average) and Max Stress (max). The effect of nanorestitution treatment on flexural strength.

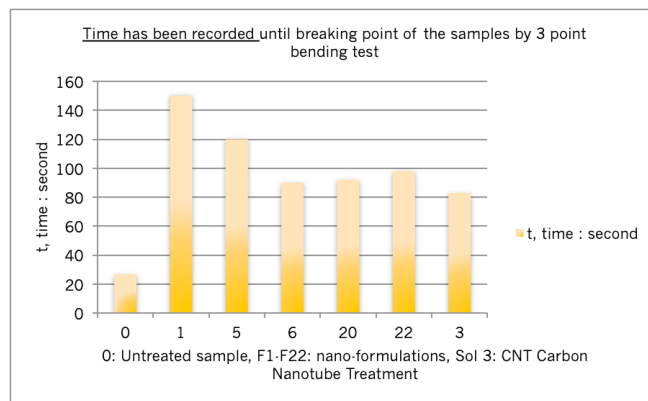


Figure 3: The effect of CNT Carbon Nanotube treatment on time, recorded until breaking point of the samples by 3 point bending test. (Sungur, 2016)

Relating to all these data, that has been experienced before, it is obvious that nanoparticles in right combinations and created formulations can evenly make big differences in terms of the durability factors such as mechanical and flexural strength for different kind of structures such as bone and limestone. (Gerhardt and Boccaccini, 2010), (Fernández et al., 2016), (Zarifah et al., 2016), (Jones et al., 2006), (Thian et al., 2007), (Sungur, 2016).

3.4. How to Offer Innovative Formulas for Next Generation Solutions

Table 1. New Formulated Hybrid Nano-composites To Go Further

Hybrid Prototype	1 st Treatment	2 nd Treatment	Compressive Strength (N/mm ²)
Prototype 1	Ca(OH) ₂	SiO ₂	evaluation criteria for 1
Prototype 2	Ca(OH) ₂	HAp (Hydroxyapatite)	evaluation criteria for 2

Prototype 3	SiO ₂ nanosilica	HAp (Hydroxyapatite)	evaluation criteria for 3
Prototype 4	SiO ₂ nanosilica	Ca(OH) ₂ nanoparticle	evaluation criteria for 4
Prototype 5	HAp (hydroxyapatite)	SiO ₂ nanosilica	evaluation criteria for 5
Prototype 6	HAp (hydroxyapatite)	Ca(OH) ₂ nanoparticles	evaluation criteria for 6
Prototype 7	SiO ₂ nanosilica	SAE	evaluation criteria for 7

Table 2. 2 Step Idea (1st step to fill the porosity with nanoparticles and 2nd step to create functional surface coating for a solution against a pre-defined problem such as freeze thaw cycles in architecture)



4. Conclusion

Nanotech and innovative design technologies has been created a huge effect on science world with all the reinforcement and enhancement effect criterias in lots of studies has been told above. Now, the question is how to go further and how to adopt these innovations in interdisciplinary area in order to find new solutions for unresolved issues in practice for architecture and engineering applications. In this research topic, regarding to doctorate thesis study that has been carrying out in Politecnico di Milano Department of Architecture and Urban Studies (DASTU), cultural heritage building preservation case is one of the major aims, so, in order to create an innovative solution related to well known problem of freeze thaw cycles in CH buildings, the nw offer of next generation hybrid design is to make a technology transfer between the medicine and architecture, and to adopt the bone regeneration therapy issues to building preservation cases. Under the experience of the successful results that has been carried out on bone scaffold design technology and osteoporosis treatments, with the chemical and morphological composition similarities between bone and limestone (Almhdie et al., 2014), it is obvious to sum up that the innovation of nano-medical therapies are also useful for nano-architecture solutions, and this research has been inviting all the architectural science researchers to create new innovative design technologies for all the desired functionalities of engineering and architecture topics. All the innovation starts with to make the correct optimization between the chemical composition of substrate and structural morphology of the lithotype. Taking into account with the criteria of porosity, colloidal stability and transport mechanism; it is possible to make new sustainable interdisciplinary innovations continuously.

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