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SCIENCE and ART: A Future for Stone

Proceedings of the 13th International Congress on the Deterioration and Conservation of Stone – Volume II

Edited by
John Hughes & Torsten Howind

SCIENCE AND ART: A FUTURE FOR STONE

PROCEEDINGS OF THE 13TH INTERNATIONAL CONGRESS ON THE DETERIORATION AND CONSERVATION OF STONE

6th to 10th September 2016, Paisley, Scotland

VOLUME II

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John J. Hughes and Torsten Howind

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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

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EUROPEAN PROJECT
"NANO-CATHEDRAL: NANOMATERIALS FOR CONSERVATION OF EUROPEAN ARCHITECTURAL HERITAGE DEVELOPED BY RESEARCH ON CHARACTERISTIC LITHOTYPES"

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Abstract

Europe has significant cultural and environmental diversity together with an exceptional ancient architecture and built environment. From the point of view of conservation, this architectural excellence and heritage may present degradation problems related to the variety of stone materials used for their construction. In the present project five different medieval cathedrals and a contemporary opera theatre were selected as they may be considered as representative of both different environmental conditions and types of stones (limestones, sandstones and marbles) in Western Europe. The project aims at developing new materials, technologies and procedures for the restoration and conservation of stone in ancient cathedrals and monumental buildings, with a particular emphasis on the preservation of the originality of the building materials and on the development of tailor-made approach to tackle the specific problems. The original materials will be analysed and classified, evaluating their connection with historical exploitation of quarries as a source of building materials. Nanomaterials suitable for the consolidation and protection of stones will be developed aiming at providing the best technological answer for the preservation of different types of stones, according to porosity and mineralogical and chemical features. The exploitation of the project will bring about the adoption of best practices for the preservation of the cathedrals and high quality buildings by selecting the most advanced nanotechnologies.

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Keywords: architectural heritage, nanomaterials, stone conservation, consolidation, protection

1. Introduction

1.1. Project "Nano-cathedral"

In the framework of the EC Horizon 2020 Nano-Cathedral project[1] launched in 2015, nanomaterials for the preservation of stone based monuments have been designed as a result of a collaborative effort of European research Centers, companies involved in the development and production of engineered inorganic nanoparticles, Conservation Institutions and Foundations managing monumental buildings. The general objective of the three-year project is the design, production and evaluation of different types of inorganic and polymeric nanoparticles as well as nanoparticles based formulations, to be applied as protective and/or consolidation treatments onto different lithotypes on European monuments characterized by a variety of environmental exposure conditions. In particular, the Cathedral of Pisa (Italy) and the Cathedral of Santa María of Vitoria-Gasteiz (Spain) are representative of south European "Mediterranean" climate in coastal and continental regions, respectively; the Sint-Baafs Cathedral of Ghent (Belgium), the Cathedral of St. Peter and Mary of Cologne (Germany) and the St. Stephen's Cathedral (Vienna), are included as representative of a Central-North European climate in continental regions. Moreover, the Oslo Opera House (Norway) was considered as an example of a contemporary building cladded with white Carrara marble. The stones used for the construction of the buildings have been analysed and classified, evaluating their connection with historical exploitation of quarries as a source of building materials, thus improving the knowledge of the architectural and artistic heritage and the connections with the regional context. For this purpose a general protocol has been defined for the identification of the petrographic and mineralogical features of the stone materials, the evaluation of their state of conservation, the identification of correlations among the relevant state of decay, the material properties and the local macro and microclimatic exposure. The innovative nanomaterials, that will be developed, will be applied on stone materials taken from quarries representative of the selected lithotypes, and they will be tested before and after application of the consolidation and/or protection products to evaluate the effectiveness of the treatments, following a protocol of laboratory tests which include microscopic observations, colorimetry and spectroscopic analyses. Finally, the best formulations of consolidants and protective treatments will be applied on pilot-areas selected in each building and non-destructive tests will be carried out to monitor their effectiveness and durability.

1.2. Nanomaterials for stone conservation

Since '80s, the scientific research has been devoted to the development of nanomaterials to be applied in a wide range of fields, including the conservation of Architectural Heritage. Compared to traditional materials and methods, the innovative nanomaterials show enhanced effectiveness in their main properties as their higher surface area make them more reactive. Regarding the class of stone consolidants, one of the first synthesized

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[1] H2020 Grant Agreement N.646178; NMP-2014-2015/H2020-NMP-2014-two-stage

nanomaterial is nanolime, that is a water or alcoholic dispersion of $Ca(OH)_2$ nanoparticles. Nanolime has been used for the consolidation of calcareous stone and wall paintings, since it presents different advantages compared to traditional limewater: higher reactivity, deeper penetration in the substrate, reduction of carbonation time and higher stability (Chelazzi *et al.* 2013, Rodriguez-Navarro *et al.* 2013). Different commercial nanolime and dispersions of nano-SiO_2 are available on the market and their use is becoming more common among restorers, despite nowadays the most used consolidants are alkoxy-silane and oligomers. In order to overcome the drawback of alkoxy-silanes related to the formation of cracks of the silica gel, particle-modified consolidants, based on the introduction of different nanoparticles in pre-polymerized tetraethoxysilane, have been proposed (Miliani *et al.* 2007, Kim *et al.* 2009). Another interesting nano-consolidant is the one proposed by Verganelaki, which consists in the incorporation of nanoparticles of amorphous calcium oxalate monohydrate in TEOS to form a crack-free nanocomposite, with a good penetration depth inside the substrate, able to increase the strengthening properties of calcareous building stones and cement mortars (Verganelaki *et al.* 2015). Nanotechnology is also applied for the synthesis of protective treatments for stone materials, realized by adding different nanoparticles (SiO_2, SnO_2, Al_2O_3) inside polymeric media (poly(methyl methacrylate), functionalized perfluorinated polyether and polyalkylsiloxane) to increase the stone surface roughness (Manoudis *et al.* 2009, Facio and Mosquera 2013). These nanocomposites are able to confer super-hydrophobic (water contact angle > 150°) and self-cleaning properties to the stone. Moreover, TiO_2 nanoparticles have been used for the synthesis of self-cleaning consolidants and protective treatments because of their photocatalytic property to promote the degradation of inorganic and organic pollutants and their ability to create superhydrophilic surfaces (Munafò *et al.* 2015). Among TiO_2-based self-cleaning coatings for Cultural Heritage stone surfaces, two different categories can be identified. The first one includes hydrophilic nano-TiO_2 dispersions (Quagliarini *et al.* 2013), whereas the second one comprises hydrophobic and superhydrophobic nanocomposites (Kapridaki *et al.* 2014).

The results of the current and more recent literature demonstrates the potential of nanostructured consolidants and protective treatments for the conservation of architectural heritage, since they can overcome the open challenges related to durability, adhesion on the substrates, effectiveness and transparency issues.

2. Survey on commercial and research stone consolidants and protective coatings

One of the activities of the Project concerns the realization of a survey to setup a database of the most applied commercial products and the most relevant research products from the current scientific literature in Europe for the consolidation and the protection of natural decayed stones. The collected data are coming from the Project Partners on the basis of their professional and research experience and the elaborated data are strictly connected to this provenance; therefore, the database is not an exhaustive collection of all the commercial or research products available. Among commercial products, the total number of different consolidant materials is 37. They can be divided in three main chemical classes: alkoxy-silane and oligomers, acrylics and low molecular weight inorganics. 12 of them contain nanoparticles in the formulation, in particular $Ca(OH)_2$, SiO_2, ZrO_2, Al_2O_3 (Fig. 1). Regarding the dispersing media, the most used ones are organic solvents. Among commercial products, the total number of different protective coatings is 21, 2 of which have antifouling properties. They can be divided in 5 chemical classes: alkyl-alkoxy-silane oligomers, alkyl-aryl-polysiloxanes, fluorinated or partially fluorinated polymers, low molecular weight inorganics and vegetable polysaccharides. Among them 5 contain nanoparticles in the formulation, in particular Ag, SiO_2, TiO_2, ZnO nanoparticles (Fig. 1). Organic solvents are the most used in the formulations.

Among research products the total number of consolidants is 39, 2 of which have also antifouling properties. They can be divided in 4 main chemical classes: alkoxy-silane and oligomers, acrylics, low molecular weight inorganics and products of biomineralization. A wide range of nanoparticles have been used in the formulation but nano-SiO_2 is the most used one. Organic solvents are the most used in the formulations, which have been applied on different stone substrates, following different application methods. The total number of protective coatings is 27, 4 of which show antifouling properties and 2 of which show both properties. They can be divided in 4 main chemical classes: alkyl-alkoxy-silane oligomers, alkyl-aril-polysiloxanes, acrylic polymers, fluorinated or partially fluorinated polymers, oxalates, low molecular weight inorganics and aliphatic polyesters. Also for research protective coatings, a wide range of nanoparticles have been used in the formulation among which nano-TiO_2 is the most used one. Organic solvents are the most used in the formulations, which have been applied on different stone substrates, following different application methods.

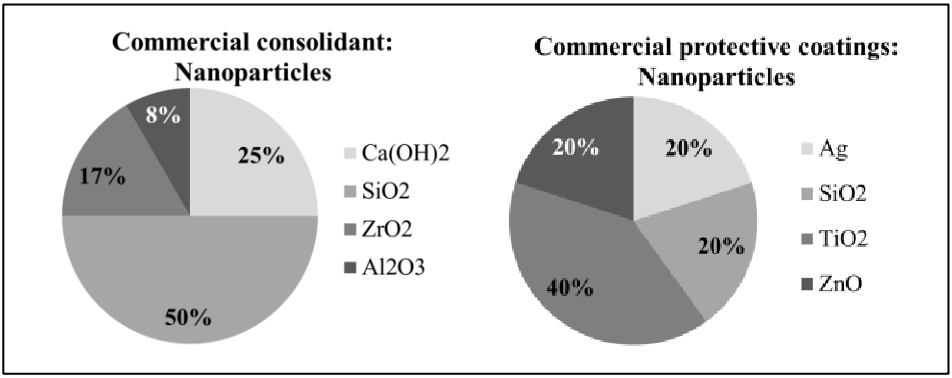

Fig. 1: Nanoparticles present in commercial consolidants (left) and protective coatings (right).

3. Selection of lithotypes

For each cathedral one lithotype has been selected (except for Cathedral of Cologne, for which two lithotypes have been selected) taking into account its petrographic properties and its representability for the building but also with respect to the European context, to grant a large scale application of the project results. The selected lithotypes are summarized in Tab. 1.

Tab. 1: Selected lithotypes for the full characterization and application of consolidation and protection formulations.

Building	Stone name	Lithotype
Cathedral of Vitoria-Gasteiz	Ajarte	Fossil limestone
Cathedral of Ghent	Balegem	Sandy limestone
Cathedral of Cologne	Obernkirchen	Sandstone
	Schlaitdorf	Sandstone
Cathedral of Vienna	St. Margarethen	Calcareous arenite
Cathedral of Pisa and Oslo Opera House	Carrara marble	Marble

4. Innovative consolidants and protective coatings

4.1. Aqueous Nanocalcite dispersions as consolidant

Nanoparticles of calcium carbonate are produced by a novel process involving colloidal particle stabilisation with either citrate or a block copolymer of poly(ethylene oxide) with poly(citrate). The optimisation of the synthetic procedure for the aqueous nanoparticle dispersions is targeting the smallest achievable particle size, since these nanocarbonates (calcite, vaterite which is a polymorph of calcium carbonate) are expected to penetrate to some extent into the porous network of degraded calcareous stones. The citrate anion plays a key role both as a nanoparticle stabiliser (it adsorbs efficiently onto the surface) and as a promoter of adhesion of the nanoparticle onto the calcareous stone surface (or inner pore surface) thanks to its ability to “chelate” the Ca^{2+} ion. Combinations of the obtained nanocalcite with conventional silane consolidants (e.g. based on TEOS) will also be explored, as it is expected that a “nanoparticle-modified consolidant” may improve the performance of simple TEOS-based treatments in terms of achieved stone cohesive strength and lower long-term damage (e.g. by shrinkage-induced micro-cracks in the silica-like material resulting from TEOS-based consolidation).

4.2. Water-borne polymeric and hybrid polymer/inorganic nanoparticle formulations

New self-stabilized amphiphilic or hydrophobic copolymers are being synthesized, as components of either consolidant or protective formulations, respectively. In particular, the composition and structure of the (acrylic) copolymers are designed to provide one or more of the following features:

i) Enhanced stability to photo-oxidative aging, by inclusion of comonomer units bearing the 2,2,5,5-tetramethylpiperidine (or Hindered Amine Light Stabilizer, HALS) group in the side chain;
ii) A combination of acrylic and methacrylic comonomers (e.g. methyl methacrylate, butyl acrylate) in a mole ratio providing the required balance of thermal and mechanical properties, while keeping the polymer photooxidative sensitivity at a minimum;
iii) Side-chain semifluorinated comonomers for enhanced hydrophobicity and chemical stability;

iv) One terminal hydrophilic short "block" of either poly(acrylic acid) (PAA) or poly(ethylene oxide) (PEO) to provide the polymer particle with the required colloidal and storage stability, without the addition of low molecular weight surfactants.

Depending on the expected performance and material requirements, the aqueous colloidal dispersions are synthesised according to one of the following two methods:

a) Conventional free radical emulsion polymerisation, yielding a high molecular weight random copolymer with uncontrolled comonomer distribution and requiring addition of a molecular surfactant for colloidal stabilisation during and after synthesis;
b) The so-called "ab initio" controlled RAFT (Reversible Addition Fragmentation Transfer) polymerisation, which may be performed in "soapless" conditions (without added surfactant) and leads to the formation of amphiphilic block copolymers, self-assembling into polymer nanoparticles of controlled size (typically within the 50-150 nm range). In this case the presence of a hydrophilic PAA or PEO block is mandatory, and may contrast the hydrophobic contribution of the remaining polymer structure. However, the PAA block may contribute to "anchoring" the polymer either to the stone surface, thus providing consolidation effectiveness, or to inorganic nanoparticle surface in hybrid formulations used as protectives. An advantage of the PEO block, on the other hand, is its inertness towards carbonatic stones and its photodegradation behaviour leading to fragmentation and eventually self-removal of this hydrophilic component from the polymer layer.

The specific contributions of these structural features to the ultimate polymer properties are assessed by a broad range of analytical techniques to fully characterize the relevant structural (by spectroscopies), morphological (by Dynamic Light Scattering and electron microscopy) and film surface (by contact angle, Zeta potential, and ATR-FTIR analyses) features.

5. Conclusions

The main objectives of this Project are: innovation in materials technology and rationalization of the conservation policy, affording a renewed knowledge of the complex system - treatment/stone substrate and of the durability threshold of these treatments.

The wide experience and literature on the nanostructured materials in the field, the multidisciplinary approach and the inclusion of industrial partners – Colorobbia Consulting Srl, Chem-Spec srl, Tecnologia Navarra de nanoproductos sl – will grant the possibility to set-up new affordable conservation treatments.

In the first semester of the Project, a decisive state of the art about the use of nanotechnologies for the consolidation of stone materials was carried out, assessing nano-SiO_2 and nanolime as the most used nanostructured materials. In the field of protection and water-repellent treatments for stone surfaces, TiO_2 and ZnO nanoparticles are the most employed in dispersions or formulations.

In the framework of this Project, some different new nanomaterials have been already designed and prepared. An important achievement is the set-up of the new synthetic procedure for nanocalcite which will be used and tested as simple dispersion, which can easily penetrate the porosity of calcareous stone materials, or will be used as an additive in particle modified consolidants (i.e. modified TEOS) and improve the adhesion of the system to the crystalline substrate. New self-stabilized amphiphilic or hydrophobic copolymers have been already synthesized to be used as protective treatments or in hybrid system covering nanoparticles of different nature.

A short testing protocol will be carried out in the following months to assess the most promising nanomaterials. Actually, the Technology Readiness Level of the project should be at least 5, as the developed technologies will be validated in lab and *in situ*, that is on the selected monuments.

Aknowledgements

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NEW POLYMER ARCHITECTURES FOR ARCHITECTURAL STONE PRESERVATION

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Abstract

A series of multifunctional polymeric systems have been designed, synthesized and their effectiveness in modifying the surface properties of different stone types have been evaluated. Both the synthetic strategy and the design of the macromolecular structures are aimed at achieving maximum flexibility in the introduction of structural features that are required to provide the resulting polymers with a range of potential properties. For this purpose, the controlled free radical polymerization of acrylic monomers by the so-called RAFT (Reversible Addition Fragmentation Transfer) technique has been adopted to obtain amphiphilic block copolymers. These may be used either as such in the modification of aqueous dispersions of inorganic nanoparticles (silica, titania, zirconia, zinc oxide among others), resulting in hybrid nanocomposite treatment materials, or as self-assembling reactive precursors for *ab initio* emulsion polymerizations, leading to the formation of colloidal aqueous dispersions of nanostructured multifunctional polymer nanoparticles. Among the innovative features of the polymers under investigation, the self-stabilisation against photooxidative degradation is worth mentioning as the durability of organic polymers is a well-known open issue in conservation. To achieve enhanced stability, free radical scavenging groups such as Hindered Amine Light Stabilizers (HALS) are introduced in the polymer structure through copolymerization with HALS derivatives. In addition, combination of polymers and UV-blocking inorganic particles (ZnO, TiO_2) are also expected to greatly enhance durability. These polymeric materials, and other presently under development, are intended as components of either protective or consolidant treatments to be tested first at a lab scale on various stones (both carbonatic and silicatic), then in situ on 5 different cathedrals distributed throughout Europe and on a contemporary opera theatre.

Keywords: block copolymer, hybrid latex, self-stabilisation, protection, consolidation

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1. Introduction

The stone materials undergo different kinds of alterations and degradation upon aging due to the different chemical, physical and mechanical characteristics of the stone and to the peculiar outdoor exposure. In the EU H2020 “NanoCathedral” project launched in 2015 five different medieval cathedrals and a contemporary opera theatre (Fig. 1) were selected as representative of both different macro- and micro-climatic conditions - continental vs. coastal; arid vs. humid - and different lithotypes - limestones, sandstones and marbles.

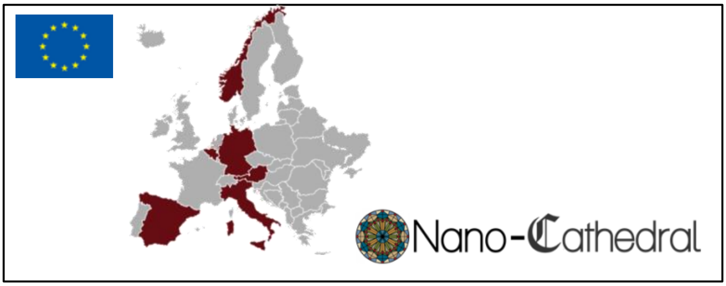

Fig. 1: Selected cathedrals within the Nanocathedral” H2020 project: Pisa (Italy) and Santa María of Vitoria-Gasteiz (Spain) exposed to south European climate in coastal and continental regions, respectively; Sint-Baafs (Ghent, Belgium), St. Peter and Mary (Cologne, Germany) and St. Stephen (Wien, Austria) exposed to North European climate in either coastal or continental regions. Oslo Opera House, dipping into the North Sea.

The project aims at providing innovative consolidant and protective products tailored for the specific stone-environment combination, while granting improved effectiveness and durability. In particular, a wide range of inorganic nanoparticles, innovative polymeric structures, and their hybrid combinations are being investigated. The best products and formulations, selected according to their performance and durability tests performed in three different laboratories and on stone specimens representative of those present in the different monumental buildings (fig. 1), will be applied during the second year of the three-year project on the participating Cathedrals for in situ evaluation.

A key requirement for *consolidants* is its effective penetration by capillarity into the stone porous network; this is often not achieved, as shown by the failure of many past consolidation treatments causing damage by formation of surface scales. Lack of chemical/physical compatibility or uncontrolled reactivity with the stone substrate is another reason of failure; poor durability of the consolidant a third one. Last but obviously not least, a consolidant material has to perform its main role of strengthening the micro-structure of the decayed stone by replacing lost original mineral bridges, partially recovering lost mechanical properties, and in some cases even converting unstable material into stable one (e.g. soluble into insoluble salts). Several reviews report on the state of art in stone consolidation (Clifton, 1980; Doehne and Price, 2010). Alkoxysilanes are currently the most commonly used consolidating materials, followed by acrylics. While the former may perform poorly due to bridging capacity limited to narrow fissures, long term shrinkage causing the formation of a secondary porosity, hydrolytic instability and poor chemical affinity with carbonatic stones, acrylics may develop better bridging properties but, as most organic polymers, their durability is poor and degradation products may be detrimental to the stone substrate.

Novel nano-materials may overcome penetration depth issues, while their extremely large surface area may promote the reactivity required to build up cohesive and adhesive forces. Nano-lime systems, also applied in combination with alkoxysilane treatments, have shown encouraging results, although the penetration and durability of such treatment has not been clearly demonstrated yet (Daehne and Herm, 2013). The so-called (nano)particle modified consolidant (PMC), typically based on tetraethoxysilane (TEOS) formulations with silica nanoparticles, can reduce the internal stone damages caused by the shrinkage and cracking during sol-gel condensation of TEOS (Ksinopoulou *et al.*, 2016). However, shortcomings are still related to the hydrolytic sensitivity and poor control of the time evolution of the consolidant nanophase during the sol-gel process. On the other hand other types of inorganic nanoparticles (e.g. Ti, Zn, Al, Si oxides or hydroxides) and hybrid organic-inorganic systems have been much less extensively investigated, although they may provide additional useful features such as biocidal (Gómez-Ortíz *et al.*, 2013) and self-cleaning properties, synergistic mechanical reinforcement, hydrophobicity, etc..

When dealing with hydrophobic *protection* the main open issues are durability inertness towards the stone substrate and lack of undesired aesthetic modifications upon and after application. Even in this case the limited durability of organic polymers is raising major objections, among conservators, against their application, although they are undoubtedly superior materials in providing hydrophobic and even self-cleaning surfaces. Even in this case, however, novel polymeric, hybrid or nanocomposite systems may provide solutions to overcome these drawbacks and even introduce additional useful features such as e.g. biocidal activity (van der Werf *et al.*, 2015). Among the various materials under development within the H2020 Nanocathedral project, here the design and synthetic approach to novel polymeric structures and their water based formulations will be presented, along with the preliminary results concerning their characterization and the evaluation of their performance and durability.

2. Approach and Results

2.1. Design of multifunctional polymer structures

The underlying criteria for the newly developed polymers are:

a) A synthetic approach that may allow easy adaptation of the polymer structure according to the specific requirements of either consolidation or protection;

b) Self-dispersibility in water (i.e. without added low molecular weight surfactants) in the form of nanoparticles with controllable (< 100 nm) size, for solvent-free application and effective penetration within the porous stone network;

c) Functional groups for enhanced durability, water repellency, specific interaction and binding with inorganic nanoparticles (for nanocomposite treating materials) and with the stone substrate, respectively.

For such purposes, a synthetic scheme for multifunctional acrylic copolymers based on the controlled RAFT (Radical Addition–Fragmentation-Transfer) free radical polymerization is adopted. The relatively recent RAFT technique (Wang A.R. and Zhu S., 2003) has become very popular in recent years due to its tolerance towards most functional groups (thus allowing the synthesis of multifunctional polymers) and solvents (from hydrocarbon to water). Besides, the so-called “ab initio” RAFT emulsion polymerisation, may be performed in “soapless” conditions (without added surfactant) by using amphiphilic RAFT mediators, leading to the formation of amphiphilic block copolymers self-assembled into nanoparticles of controlled size (typically 50-150 nm) (Chenal *et al.*, 2013).

With the above approach, water-based polymer dispersions with controlled composition and a range of functional groups have been prepared, for desirable properties such as:

- colloidal stability (for extended shelf life and easy application), by using a RAFT mediator leading to the formation of polymers with a short “block” of either poly(acrylic acid) (PAA) or poly(ethylene oxide) (PEO) at one chain end;
- adhesivity by incorporation of comonomers with either Ca^{2+} binding (e.g. carboxylate, for carbonatic stones) or sol-gel reactive (e.g. trialkoxysilyl groups for specific bonding to silicatic stones) functional groups;
- film cohesivity, by balancing the main copolymer composition (methyl methacrylate/butyl acrylate) for a polymer glass transition, T_g, slightly below room temperature, while keeping the polymer photooxidative sensitivity at a minimum;
- self-stabilisation against photo-oxidative aging, by incorporation of HALS group in the side chain (stabilisation against UV-induced photooxidation is based on a cyclic deactivation of photogenerated free radicals and peroxiradicals, followed by regeneration of the free-radical scavenging nitroxyl-amine active species.
- water repellency, by introduction of semifluorinated comonomers (in progress).

2.2. *Polymer synthesis*

The general synthetic scheme starts with an amphiphilic trithiocarbonate RAFT mediator extended with a short hydrophilic oligomer through controlled free radical polymerization. The obtained RAFT-active amphiphilic oligomers (Fig. 2) can then be used as block copolymer precursors of functional polymer nanoparticles (Fig. 3).

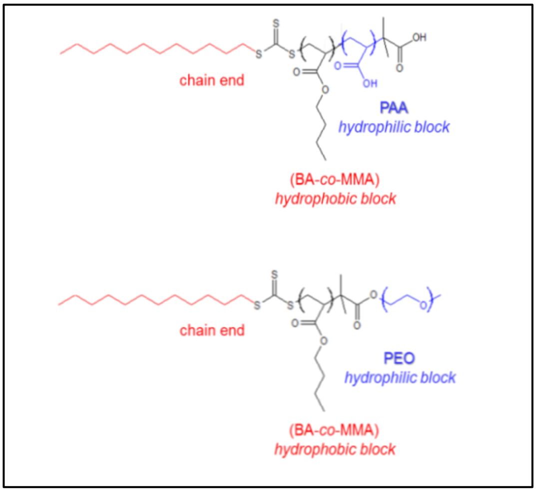

Fig. 2: RAFT-active amphiphilic block copolymer precursors.

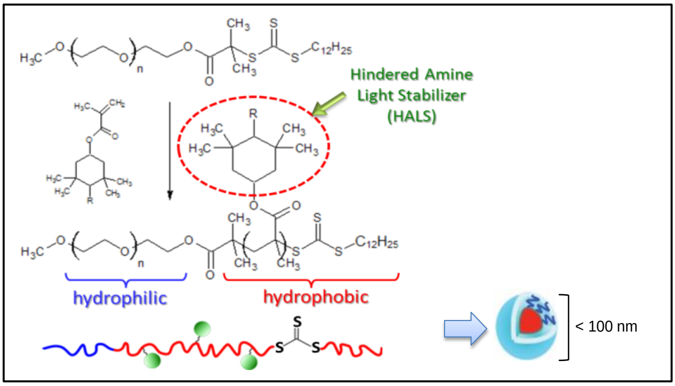

Fig. 3: synthetic scheme for self-stabilized multifunctional block copolymer nanoparticles by ab-initio RAFT emulsion polymerization of amphiphilic precursors.

3. Materials and characterizations

3.1. Latex Polymers

A selection of the functional polymer dispersions (polymer latexes) prepared during the first year of the project is listed in Tab. 1. Macro-RAFT is the alkyl-dithiocarbonate terminated oligo (acrylic acid) (PAA-TTC) or oligo(ethyleneglycol) (MPEG-TTC) of Fig. 2, used as a reactive surfactant and RAFT mediator in the ab initio emulsion polymerization of the butyl acrylate/methyl methacrylate (BM) mixture. The polymer latex acronyms indicate the amount of hydrophilic PAA or MPEG block (1 to 5 wt.- %) and of the HALS comonomer (1 and 3 wt.-% in H1 and H3 samples, respectively).

Tab. 1: Water borne polymer particles.

Polymer Latex		**Macro-RAFT** wt.-%	**PMPMA** wt.-%	**Solids content** wt.-%	**Particle size** nm
BM-PAA5-H1	(DS4)	PAA-TTC	1	7.8	170
BM-PAA3-H1	(DS7)	PAA-TTC	1	9.0	143
BM-PAA1	(DS10)	PAA-TTC	//	9.1	188
BM-PAA1-H1	(DS11)	PAA-TTC	1	9.2	55
BM-PEG5	(DS9)	MPEG-TTC	//	8.0	79
BM-PEG5-H1	(DS12)	MPEG-TTC	1	7.9	181

The latexes were cast to clear films, and after dilution to 1 wt.% solids were applied by capillarity to Carrara marble and Schleitdorf sandstone (Cologne), respectively, to a nominal 1 μm-thick coating (actually thinner due to absorption into the porous stone). The water contact angles (Tab. 2) and the surface Zeta potential data (Fig. 4) show that even at low concentration and without structure optimisation, these relatively hydrophilic materials are effective hydrophobic modifiers.

Tab. 2: Static water contact angle on polymer films and treated stones.

Polymer Latex		**Smooth polymer film**	**Sandstone**	**Marble**
		deg	deg	deg
Untreated stone			35.2 ± 2.3	35.2 ± 2.0
BM-PAA1	(DS10)	90.0 ± 2.0	105.3 ± 3.5	99.4 ± 5.4
BM-PAA1-H1	(DS11)	86.5 ± 0.8	104.5 ± 5.6	81.7 ± 7.0
BM-PEG5	(DS9)	91.6 ± 0.2	100.5 ± 8.6	67.7 ± 7.4
BM-PEG5-H1	(DS12)	97.2 ± 0.9	113.9 ± 5.8	99.8 ± 3.8

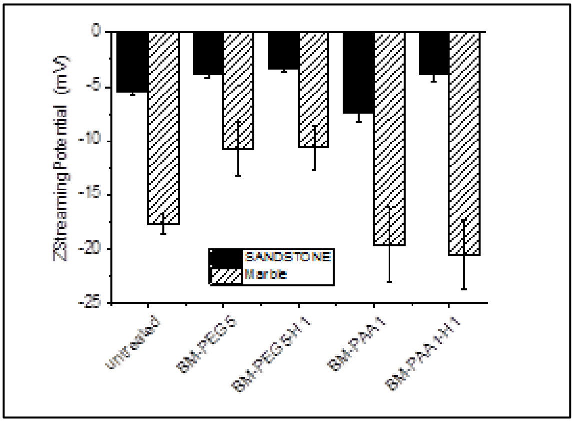

Fig. 4: ζ potential of uncoated and coated stone surfaces (measured with the Anton PAAR SurPASS® Electrokinetic Analyser).

3.2. *Ageing tests*

The FT-IR spectra of fig. 5 were recorded on cast films of selected polymers (DS#, as listed in Tab. 1) and of their nanocomposites with TiO_2 nanoparticles (DS#n), before and after the first 250 hours of simulated solar irradiation (Hereus Suntest CPS solar box, Xenon lamp, 300 nm cutoff filter, 750 W/m^2). The preliminary results indicate that:

- After 250 hours of ageing only a slight oxidation is detected from the appearance of weak OH absorptions at 3220 cm^{-1} and of a shoulder at 1640 cm^{-1} due to chain-end double bonds (compare DS9 in Fig. 5a, and DS10 in Fig. 5b, before and after agieng).
- The HALS moiety inhibits the oxidation phenomena, as shown by the further reduction of the weak OH absorption at 3220 cm^{-1} (compare DS12 with DS9 in Fig. 5a, and DS11 with DS10 in Fig. 5b)

- The photocatalytic action of TiO_2 promotes polymer oxidation phenomena (compare DS9 and DS9n in Fig. 5a) as shown by the growth of a broad absorption above cm^{-1} due to formation of hydroxy groups, irrespective of the presence of HALS groups (compare DS12 and DS12n in Fig.5a).

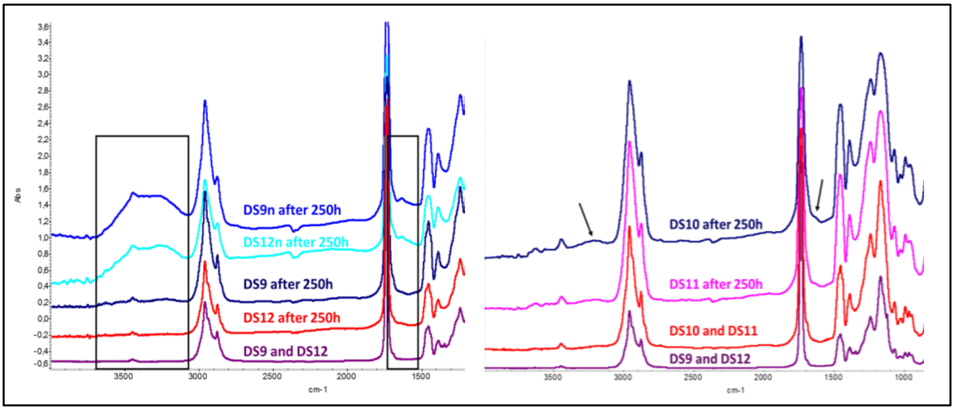

Fig. 5: FT-IR transmission spectra of films on silicon wafer.

4. Conclusions

A range of amphiphilic block copolymers and of self-stabilized, surfactant-free colloidal polymer dispersions (polymer latex) with small particle size (< 100 nm, for improved capillary absorption into the stone porous network) and reactive functional groups (carboxylate, for polymer anchoring onto stone substrates or inorganic nanoparticles) have been synthesized by means of the RAFT controlled polymerization method.

The amphiphilic block copolymers may be useful as modifiers of inorganic nanoparticles (ZnO and TiO_2 for protection, calcite, ZrO_2 and hydroxyapatite for consolidation) and as precursors of multifunctional latex particles or water-borne nanocomposite materials. Encouraging results have already been obtained from preliminary tests of application of the colloidal polymer dispersions onto sandstone and marble different stone samples (, respectively). In particular, very low amounts of applied polymer are sufficient to make the stone surface hydrophobic.

Aging tests have confirmed the foreseen stabilizing effectiveness of the HALS groups introduced by means of functional comonomers. On the other hand, the photocatalytic activity of embedded TiO_2 nanoparticles was shown to cause, as expected, accelerated degradation of the polymer matrix in nanocomposite films. Finally, a better understanding of the stone-polymer and stone-nanoparticle interaction and distribution at and within the porous stone surface may be achieved thanks to a combination standard (water absorption, water vapour permeability, contact angle) and less conventional techniques; among them, the Zeta potential may provide useful insights on the effectiveness of a treatment and on the evolution of the treated stone surface upon aging.

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