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Polyethylene glycol oligomers as siloxane modificators in consolidation of carbonate stones

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Abstract: The overall performance of alkoxysilanes as stone consolidants is constrained by stone mineralogy (particularly in the carbonate varieties) and by their tendency to crack during drying. In an attempt to overcome these problems, polyethylene glycol "chains" with two carboxylic acid end-groups (PEG-CA) were introduced in siloxane sols obtained by sol-gel chemistry using tetraethoxysilane (TEOS) as precursor. Different pre-condensation degrees (by varying the stirring times of sol-gel reaction: 10 min, 2, and 24 h) and PEG-CA chains with different molecular weights were studied as variables affecting the initial efficacy of the consolidants when applied into a limestone. The sol containing siloxanes with the lowest pre-condensation degree (10 min stirring) was quite susceptible to the carbonate media and thus a poor consolidation was achieved. The sol with the highest pre-condensation degree (24 h stirring) together with the PEG-CA chains with intermediate molecular weight produced significant and uniform strength gains along the stone depth. The consolidation also showed to be highly dependent on the molecular weight of the PEG-CA chains, the PEG-CA with highest molecular weight produced a non-uniform strength increase with potential harmful side effects. The results confirmed the role of carboxylic acid end-groups as efficient sol-gel catalysts and their ability to be incorporated into the silica matrix in the presence of carbonate stone.

Keywords: carbonate stones; consolidation; efficacy; PEG; POC-16; TEOS.

Introduction

Carbonate based stones, particularly limestones, were widely used as construction materials to build monumental and non-monumental structures throughout Europe. Nowadays, several of these structures (as well as respective sculptures or other forms of art) are regarded as built immovable cultural heritage because of their historical, religious, cultural, scientific, or esthetic significance.

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The decay of carbonate stones is a threat to the survival of such important built heritage. The associated loss of stone cohesion and consequent loss of stone material can lead into a reduction of artistic and historic value and eventually into a loss of structural integrity. Therefore, consolidation actions are often indispensable.

A stone consolidant shall be able to penetrate into the stone (until undamaged zone) and must provide cohesion to the stone in depth, without creating significant heterogeneities between inner and outer zones, to avoid harmful side effects.

The penetration and ability to provide a uniform cohesion in depth depend mainly on the nature of the stone, stone absorption properties, application time and procedure, and nature of the consolidant.

Some of the intrinsic properties of TEOS-based consolidants make them the most used products for the consolidation of stone surfaces. However, when applied in carbonate stones their overall performance tends to be unsatisfactory. Alongside with the lack of affinity between calcium carbonate and hydrolyzed TEOS, the literature points out their tendency to crack during the shrinkage and drying phase as one of the main problems [1–3].

Several authors have followed different approaches to overcome these constrains. Possible routes include the use of organo-fuctional silanes [2, 4], the incorporation of various nanomaterials [2, 5, 6] and, possibly the most well established strategy, the incorporation of silicon-based organic polymers [6–10]. The latest intends to prevent the collapse of the silica gel during the drying phase by increasing the pore radius of the network, thus reducing capillary pressures. Furthermore, the incorporation of flexible segments within a brittle silica matrix also enhances ductility, increasing the ability of the material to deform under stress, preventing cracking.

Silanol-terminated polydimethylsiloxane (PDMS-OH) is the most used silicon-based organic polymer for this purpose. The successful incorporation of PDMS-OH on the silica matrix depends on the relative rates of sol-gel reactions: when TEOS hydrolysis is fast enough to provide –OH groups for the reaction with the PDMS-OH, a good dispersion of the functionalized PDMS-OH is usually achieved. Phase separation can occur in different extents depending on the reactional conditions, such as the type of catalyst and PDMS-OH molecular weight [11]. Mosquera et al. [12, 13] obtained homogeneous gels (without phase separation) from TEOS/PDMS-OH systems by introducing n-octalamine as catalyst to accelerate the rate of hydrolysis and, simultaneously, as a network templating agent. This solution enhanced the compressive mechanical strength of a biocalcareous stone composed of calcite, quartz, and feldspar [12, 13].

Within this context, our previous work addressed different TEOS-based formulations containing polyethylene glycol chains end-capped with two carboxylic acid groups (PEG-CA): decanedioic acid (SA) and 3,6,9-trioxaundecanedioic acid (TUDA) [14].

It was found that SA segregates from the silica matrix, while TUDA plays a two-fold role: before application into the stone, it acts as efficient sol-gel catalysts, promoting TEOS hydrolysis and pre-condensation; when introduced into the carbonate media, the carboxylic acid end-groups become deprotonated and allowed to condense into the siloxane network, the chains also acted as flexible spacers [14].

Only few sols showed a convenient combination of properties: good penetration ability, polymerization time, dry residue, and ability of calcite powder consolidation. The sol containing the molar ratio of 1TEOS/2.1H_2O/3.8EtOH/0.05TUDA showed an appropriate combination of characteristics [14].

The adopted systematic approach allowed to conclude that the potential applicability of the sols depends on both TEOS/TUDA ratio and siloxanes pre-condensation degree (controlled by stirring time).

The approach proposed in this paper is based on the mentioned sols and pursuits two major objectives: to study the influence of siloxane pre-condensation degree on the consolidation efficacy (initial efficacy) by varying the stirring time, and to understand the effect of PEG-CA molecular weight on the sol-gel chemistry and initial efficacy, by varying the molecular weight of these chains.

The developed sols were applied into Ançã stone, which is a very porous and homogeneous limestone, mainly composed of calcite. This variety of limestone is considered a historical stone, since it was used to build some of the most emblematic monuments in Portugal.

Experimental

Materials

The sols were prepared by using tetraethoxysilane (TEOS) (Fig. 1a) and one PEG-CA: diglycolic acid (DGA, 134 g/mol, n = 0), 3,6,9-trioxaundecanedioic acid (TUDA, 222 g/mol, n = 2), or poly(ethylene glycol) bis(carboxymethyl) ether (PEGBA, ≈ 600 g/mol, n ≈ 10), (Fig. 1b), all provided by Sigma-Aldrich and used without further purification. Ethanol (EtOH) at 96 % was used as solvent and distilled water was added to enable hydrolysis reactions. Although DGA is not a PEG-CA, for simplification purposes it will be referred as PEG-CA.

Calcite powder was obtained by grinding a marble from Vila Viçosa region (Portugal), composed of > 99 % of calcite ($CaCO_3$), for 2 min in a ring mill. To maximize homogeneity, only powders passing the sieve #63 μm were used.

The stone to be consolidated is denominated by Ançã Stone and has an open porosity of 26.8 ± 0.7 %. It shows a very fine texture and can be classified as a mudstone, essentially composed by a matrix of micrite (lime mud). Stone cubes of size approximately 30 × 30 × 30 mm were used for the application of the sols.

Preparation of sols

Sols were prepared by mixing TEOS, EtOH, water, and PEG-CA with magnetic stirring (≈ 550 rpm) at laboratorial temperature. The molar ratio of the sols was 1TEOS/3.8EtOH/2.1H_2O/0.05PEG-CA (DGA, TUDA, or PEGBA).

The influence of the PEG-CA molecular weight on the sol-gel chemistry and initial efficacy was studied by using a stirring time of 2 h.

The influence of the siloxane oligomerization degree on the efficacy of the treatment was achieved by using different stirring times (10 min, 2 h, and 24 h, plus a final ultrasonic agitation of 1.5 min) in TUDA containing sols.

The pH of the reaction mixtures was measured by using a glass electrode and a pH meter (WTW-pH330i). The given values are referred as pH′ since the measurements were made in non-aqueous systems and therefore some minor discrepancies between the pH′ and values determined based on H_3O^+ concentration may exist. Nevertheless, it seems unanimous that pH′ is the best indicator to be used in sol-gel systems [15].

Table 1 shows the designations of the prepared sols and the corresponding reactional parameters.

Polymerization conditions

The sols used to investigate the effect of PEG-CA molecular weight on the properties of the final consolidant were gellified under two different environments:

i) Inside cylindrical flasks (∅ = 30 mm) with several pinholes in the cap, to allow evaporation. The resulting materials will be referred to as xerogels.
ii) Inside cylindrical flasks (∅ = 30 mm) with several pinholes in the cap, but mixed with calcite powder. The derived materials will be referred to as calcite blends.

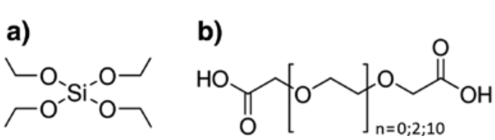

Fig. 1: Molecules of (a) tetraethoxysilane (TEOS); (b) polyethylene glycol oligomers with carboxylic acid end-groups (PEG-CA) of different sizes: diglycolic acid (DGA) with n = 0 (134 g/mol), 3,6,9-trioxaundecanedioic acid (TUDA) with n = 2 (222 g/mol) and poly(ethylene glycol) bis(carboxymethyl) ether (PEGBA) with with n ≈ 10 (≈ 600 g/mol).

Table 1: Information on the prepared sols including relevant reactional parameters.

	Designations	Stirring time	TEOS	EtOH	Water	PEG-CA	PEG-CA	pH′
Siloxane oligomerization degree	10TUDA	10 min					TUDA	3.4
	2hTUDA	2 h						
	24hTUDA	24 h	1	3.8	2.1	0.05		
Molecular weight	2hDGA						DGA	3.1
	2hTUDA	2 h					TUDA	3.4
	2hPEGBA						PEGBA	3.8

The flasks containing either sols or calcite blends were placed in a chamber at 25 °C and 70 ± 5 % R.H until mass stabilization, assumed when the decrease between two weightings at an interval of 24 h was not greater than 0.05 % of the dry residue mass.

Periodically, the sol containing flasks were gently tilted in order to determine the gelling time. The cracking tendency of the different sols was evaluated by visual inspection after stabilization of the mass of derived xerogels.

The dry residues were determined by the difference between the initial and final mass (after mass stabilization) in both xerogels and calcite blends.

The molecular structure of xerogels was investigated by attenuated total reflection infrared spectroscopy (ATR-FTIR) (Thermo Nicolet 5700) in the range 4000–600 cm^{-1} and with resolution of 2 cm^{-1}.

The preliminary cohesive ability of the sol was evaluated as follows:

After mass stabilization, the calcite blends were manually broken and a scale of five classes based on the assessment of their relative resistance was established. The classes considered were: no cohesion (complete disaggregation upon removing from the flask) (–), breaks with handling (+), easy to break with hands manually (++), hard to break with hands (+++), very hard to break with hands (++++).

This system should be intended as a simple and expedite method to assess the sols that are more suitable for stone consolidation. The methodology proved to be useful in the study of the interference of the “carbonate environment” in the sol-gel reactions while allows to predict the initial efficacy of sols [14].

Stone treatment

All sols described in Table 1 were applied into limestone samples by capillary suction during 3 h. The depth to which the stone cubes were partially immersed was around 3 mm.

The ability of the sol to penetrate within the stone pores was evaluated by periodical measurements of the height of capillary fringe during the 3 h of application (in mm).

The stone samples were weighed before and after sol application to determine the amount of absorbed sol. Thereafter, the treated samples were placed in a chamber at 25 °C and 70 ± 5 % R.H. After stabilized, the mass was taken to calculate the dry residue derived from the sols (%) and the final residue left within the stone pores (kg/m^2).

The treated stones were investigated by using an analytical scanning electron microscope (FEG-SEM: JEOL 7001F) to examine the consolidating material within the stone pores, its relationship with the substrate and the mechanism of consolidation.

The initial efficacy of the sols, i.e. the ability of the sols to provide cohesion to the stone, was quantified by microdrilling resistance (DRMS). This test provides information about the penetration depth and variation of force along depth.

In order to minimize any eventual increase in the resistance, caused by the packing of stone powder, a guide hole with 3 mm of diameter was performed all across the 30 mm of samples.

To register the force gains produced by the sols, a 5 mm diameter diamond drill bit was used to drill over the guide hole. The resultant powder was vacuumed through the end of the guide hole during the drilling.

Drills were performed at a speed rotation of 100 r.p.m. and with a 20 mm/min penetration rate.

Results and discussion

Xerogels and calcite blends

Influence of PEG-CA molecular weight

The sols containing PEG-CA with different molecular weights gelled in 6–7 days (Table 2) and the evaporation of the solvent that remained inside the matrix pores led to their natural contraction until the formation of transparent xerogels (Fig. 2).

At the pH′ range used in this work, PEG-CA carboxylic end-groups were not expected to deprotonate, not being the chains incorporated into the sol-gel matrix of the produced xerogels. In fact, the comparison between ^{29}Si-NMR spectra of TUDA containing xerogels and calcite blends [14] revealed that PEG-CA chains were not incorporated into the silica matrix when gellification occurred inside inert flasks. Contrarily, when gellification occurred in carbonate media, at higher pH′, PEG-CA become incorporated into the matrix, thus acting as spacers. The cracks observed in the xerogels represented in Fig. 2 are related to the different capillary pressures at the liquid-vapor interfaces.

Xerogels ATR-FTIR spectra are exhibited in Fig. 3. The major peaks identified in all spectra were attributed to the silica network, produced from TEOS hydrolysis and silanols condensation. The Si–O covalent bonds vibrations appeared between 1200 and 1000 cm^{-1}: the well-defined peak around 1040 cm^{-1} and the broadening around 1200 cm^{-1} were associated to the transversal and longitudinal optical modes of the Si–O–Si asymmetric stretching vibrations, respectively [16]. The Si–O–Si symmetric stretching vibrations were observed at 790 cm^{-1}, whereas the silanol Si–O stretch vibrations appeared around 940 cm^{-1}.

Table 2: Characteristic values related to the potential applicability of the sols containing PEG-CA with different molecular weights.

	2hDGA	2hTUDA	2hPEGBA
Flask			
Gelling time in flask (days)	6	6	7
Dry residue in flask (%)	19.2	22.7	22.3
Calcite powder			
Dry residue in powder (%)	19.2	21.3	12.6
Cohesion	+++	+++	++
Ançã stone			
Product absorbed (kg/m^2)	5.55	5.93	4.87
Dry residue (%)	19.4	17.0	13.2
Final residue (kg/m^2)	1.08	1.01	0.64

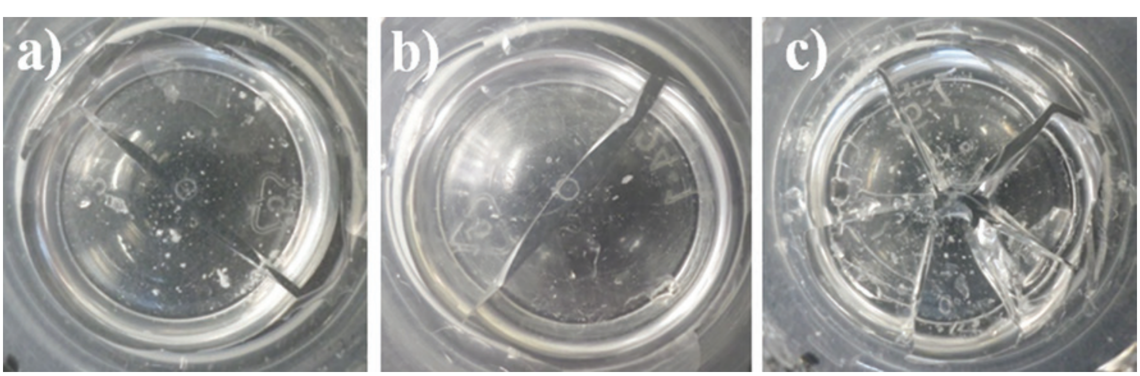

Fig. 2: Top view of the xerogels obtained from 2hDGA sol (a), 2hTUDA sol (from [14]) (b), and 2hPEGBA sol (c).

The spectra of PEGBA xerogel showed some additional, but hardly visible, peaks at 1352 cm^{-1} and around 1460 cm^{-1}. These signals were associated to the C–H asymmetric and symmetric bending vibrations from the PEGBA chains. Furthermore, a small broad at around 2900 cm^{-1} can also be ascribed to the stretching vibration of C–H [17, 18].

The overall amount of C–H bonds in xerogels with smaller chains (DGA and TUDA) is lower, so it is likely that the absence of signal at their characteristic IR bands can be related to the detection limit of the equipment. Anyway, the presence of well-defined bands near 1730 cm^{-1}, attributed to C=O stretching vibrations, confirmed the presence of PEG-CA in the three xerogels. Unfortunately, the peak at 1730 cm^{-1} also includes the contribution of C=O groups from free PEG-CA molecules that remain within the xerogel structure not being possible to extract relevant information about PEG-CA effective incorporation into the silica matrix from the relative intensities between C=O band and Si–O–Si bands.

Finally, all spectra showed a small peak around 1630 cm^{-1} and a broad band centered at 3250 cm^{-1}. Both are related to the presence of water, the first corresponding to the deformation of adsorbed water and the second to the stretching of hydrogen bonded water molecules [19].

The spectra and corresponding peaks related to the silica skeletons formed within inert flasks from the three xerogels showed similar relative intensities and complexities, suggesting equivalent silanol polymerization degrees and similar silica network structures.

According to the ATR-FTIR data, the dry residues were expected to be nearly equivalent in the three cases, as confirmed by weigh measurements (Table 2). The dry residues obtained when polymerization occurred within inert flasks were compared to the dry residues from the polymerization in coexistence with calcite powder, being possible to identify significant differences in the case of PEGBA (Table 2). Similarly to what occurs inside carbonate stone pores, the carbonate media provided by the calcite powder drastically changes the relative rates of sol-gel reactions and therefore, the polymerization paths. In sols with low pre-condensation degrees, most sol-gel reactions occurred under the influence of the "carbonate media". Since the pH′ measured in PEGBA sols (pH′ = 3.8) was higher than DGA (pH′ = 3.1) and TUDA (pH′ = 3.4) sols, a decrease of hydrolysis rate was expected [20]. As result, the pre-condensation degree was lower in 2hPEGBA, causing more sol-gel reactions to occur under the carbonate media.

The cohesion provided by the sols to calcite powder reflects such influence, the powder "consolidated" with 2hPEGBA showed to be weaker and easily broken (++), whereas the blends made with 2hDGA and 2hTUDA showed good cohesion and were hardly broken (+++).

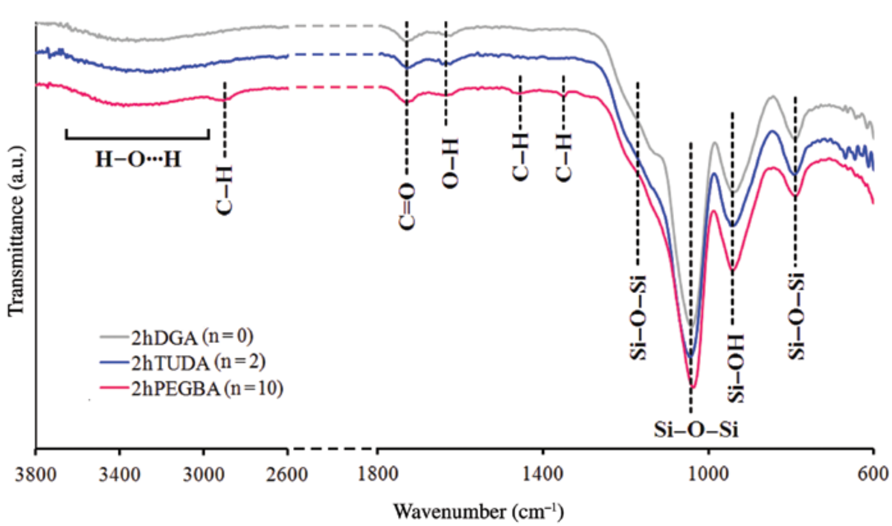

Fig. 3: ATR-FTIR spectra of xerogels derived from 2hDGA, 2hTUDA (from [14]), and 2hPEGBA sols.

Stone treatment and efficacy

Influence of siloxane pre-condensation degree

The influence of siloxane pre-condensation degree on the initial efficacy of the sol as consolidant for carbonate stone was studied by varying the stirring times of the TUDA containing sols. Since the major conditioners of sol-gel reactions were kept constant (pH′, water amount, solvent amount and nature) the stirring time was expected to act as the most important parameter.

Figure 4 exhibits the evolution of the fringe height on the stones lateral surface during the 3 h of application. The capability of the sols to penetrate within the stone pores showed to be considerably dependent on the stirring time. The sol stirred for 10 min reached the top of the stone sample (30 mm) after 2 h (11.0 $min^{0.5}$), while the sol stirred for 24 h only reached 26 mm after 3 h (13.4 $min^{0.5}$).

The stirring time naturally promotes the hydrolysis and condensation of species and, as it increases, the hydrolyzed and low molecular weight siloxane species tend to condensate into higher molecular weight siloxanes, with increased viscosity and, as demonstrated, lower ability to penetrate the stone by capillarity.

Results suggest that the amount of absorbed sol (Table 3) depends not only on the height of the capillary fringe, but also on the PEG-CA molecular weight. It is worth to mention that the height of the capillary fringe may not match with the depth where effective consolidation occurs. A selective migration of the different species according to their relative molecular weights can lead, for instance, to migration of solvent in depth, while higher molecular weight species tend to accumulate near the surface. The occurrence of this phenomenon has already been observed with other products used for consolidation [21].

Concerning the dry residues (Table 3), they were quite different, especially for the case of the 10 min stirred sol, where the obtained dry residue was less than half of the values obtained with sols stirred for longer times. Evaporation losses of alkoxysilanes during the treatment of carbonate stones is commonly attributed to the inhibition/modification of sol-gel reactions due to the "carbonate media" [14, 22]. This problem has been overcome by using pre-polymerized siloxane sols (increased stirring times), as in the case of 2hTUDA and 24hTUDA.

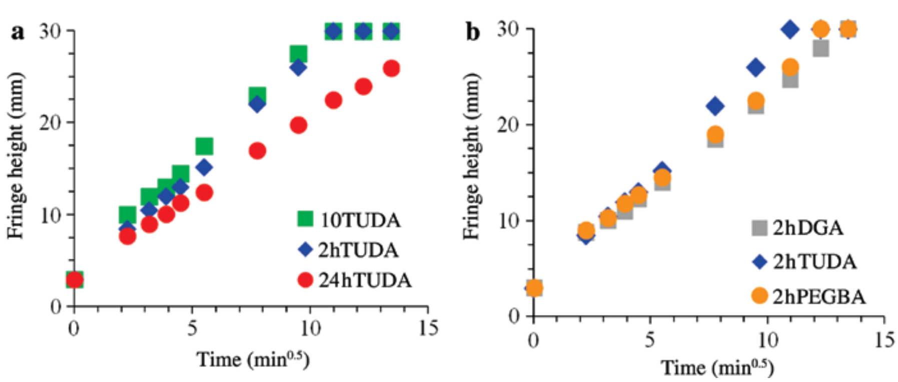

Fig. 4: Evolution of the capilary fringes during sols' application: sols with distinct pre-condensation degrees (a), sols containing PEG-CA with distinct molecular weights (b).

Table 3: Values of product absorbed, dry residue, and final residue for sols produced using different stirring times (applied in stone by capillary suction for 3 h).

	10TUDA	2hTUDA	24hTUDA
Product absorbed (kg/m^2)	4.76	5.93	5.14
Dry residue (%)	6.6 %	17.0 %	19.8 %
Final residue (kg/m^2)	0.31	1.01	1.02

The final dry residues reflect the relation between the dry residues and the amount of absorbed product. As expected the amount of final residue derived from 10TUDA is much lower than the final residue derived from sols stirred for longer times (2hTUDA and 24hTUDA). As a consequence, the consolidation is expected to be less noticeable in the first case.

Figure 5 depicts the surface of the untreated stone (a), treated stone with 10TUDA (b), with 2hTUDA (c) and with 24hTUDA (d). The presence of the consolidant, forming a uniform coating around calcite grains, bonding them, is quite evident. Despite the distinct dry residues, the concentration of consolidant material near the stone surface seems equivalent in all situations.

In contrast with the various cracks found in stones treated with commercial products and reported on literature [13], cracks were almost inexistent in the surfaces of the stones treated with the sols under study.

DRMS profiles of reference and treated stones are shown in Fig. 6. The Ançã stone revealed to be very homogeneous with an average resistance of 4.2 N.

The sol 10TUDA produced a significant increase in the stone resistance, of around 300 %, in the first millimeter of stone. In depth, the resistance gain was much more modest, around 30 %. This absence of significant strength gain can be associated to the poor presence of consolidating material.

An uniform consolidation along the stone depth may not be possible due to different reasons: i) an effective penetration cannot be achieved at all; ii) the tendency of smaller molecules (e.g. solvent, siloxane monomers, dimmers, etc.) to flow more easily and deeply than larger and more "active" molecules (e.g. highly pre-condensed species), iii) the phenomenon of reverse migration or iv) the cumulative effect of alkaline media with depth (gradual change in polymerization path).

Since 10TUDA sol presented the lowest siloxane pre-condensation level (when compared to 2hTUDA and 24hTUDA), the first two reasons were discarded. Therefore, it is likely that a joint action of both phenomena, reverse migration and change on the siloxane polymerization path in depth due to the carbonate media, were responsible for the non-uniform resistance. Reverse migration is a process that occurs when the solution that

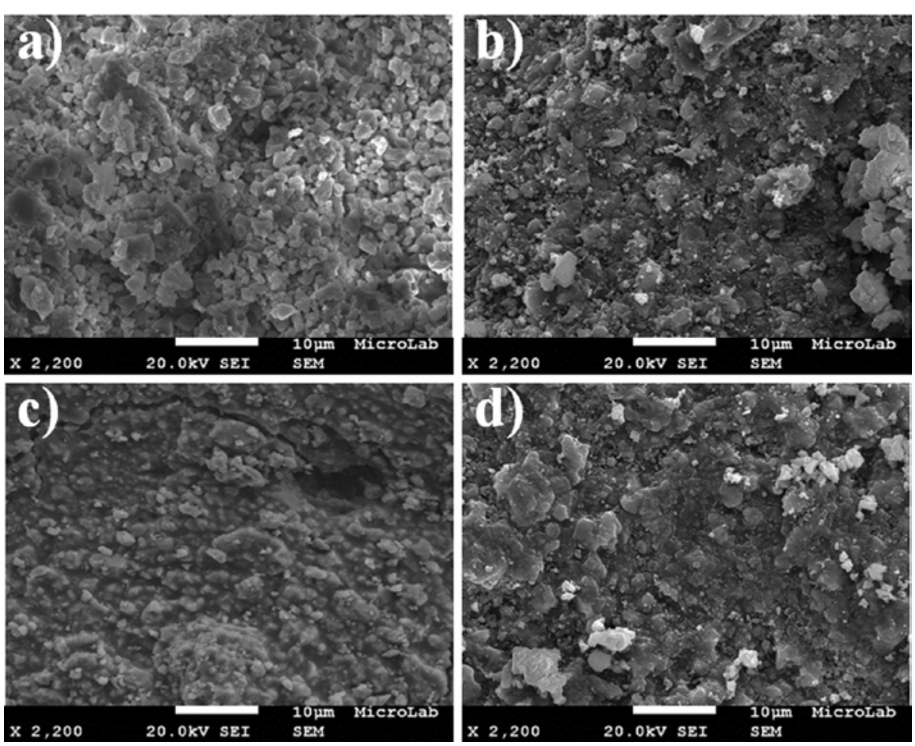

Fig. 5: SEM micrographs of the stones surfaces: untreated stone (a); stone treated with 2hDGA (b); stone treated with 2hTUDA (c); stone treated with 2hPEGBA (d).

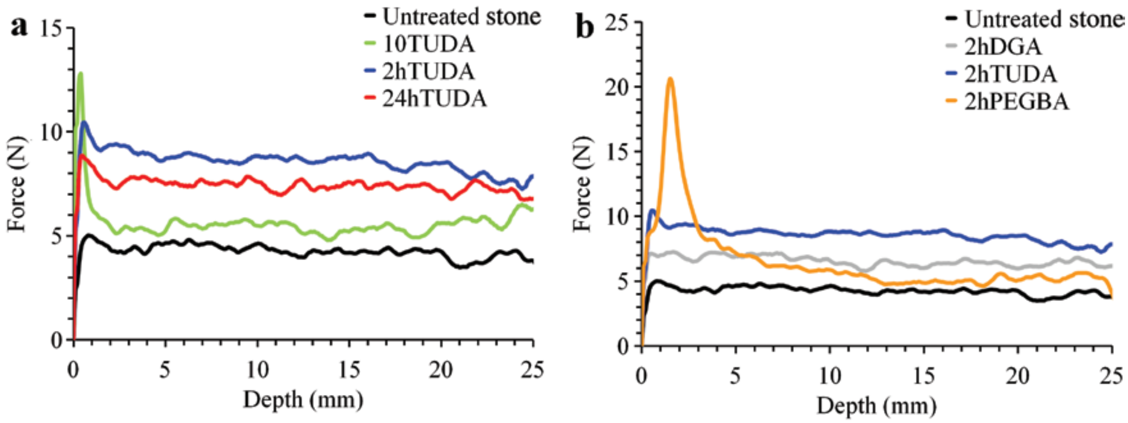

Fig. 6: Drilling resistance profiles: influence of sol pre-condensation degree on the resistance (a) and influence of the PEG-CA molecular weight (b).

has penetrated into a porous object migrates toward the surface due to solvent evaporation; the aftereffect is the over concentration of consolidant material at the outer zones [23]. The extent of this effect depends on the quality of solvent, dimension of species, solution viscosity, porous structure, and drying conditions [24]. The reverse migration of consolidant treatments has been found in stones, wooden objects, and other porous materials [23, 25, 26].

On the other hand, as mentioned before, sols with lower siloxanes pre-condensation degree (as 10TUDA) are more prone to changes in “carbonate media” and therefore this hypothesis should not be neglected. In fact, 10TUDA sol has shown to be strongly influenced by the carbonate stone alkaline environment and in a previous work it was shown that this sol was not able to provide any cohesion to calcite powder (+) [14].

In practical terms, this type of heterogeneities may induce detrimental consequences since a hard skin could accelerate some degradation phenomena [27], the detachment of the stone layer can occur and the loss of superficial material can drastically reduce the artistic value of the element, especially if carved.

The tests on samples treated with 2hTUDA and 24hTUDA revealed much more desirable profiles of drilling resistance. Apart from providing a superior resistance gain (the resistance doubled), the heterogeneity between inner and outer zones is not so prominent. This reduces the risk of failure owing abrupt variations on the mechanical resistance/physical properties along the material depth.

Despite presenting less ability to penetrate into the stone pores, sols composed by species with higher pre-condensation degrees are less prone to reverse migration and to be influence by carbonate media.

Influence of PEG-CA molecular weight

As outlined before, the ability of the sol to penetrate inside the stone pores depends on the siloxane pre-condensation degree, which in turn depends on the stirring time and on the pH′. However, the PEG-CA molecular weight can also contribute, per se, to the overall ability of the sol to penetrate. Since the stirring time was kept constant, the penetration ability of the sols, exhibited at Fig. 4b, depended on the relation between the pH′ and the PEG-CA molecular weight.

Despite presenting the lowest siloxane pre-condensation degree, PEGBA sol has the highest molecular weight and also the highest intrinsic viscosity. Therefore, the evolution of PEGBA sol capillary rise was equivalent to the evolution of 2hDGA sol, which presented a higher siloxane pre-condensation degree.

In any case all the sols showed appropriate penetration depths, according to the requirements concerning the penetration depth achieved in a consolidation action reported in literature.

For example, Sasse [28] and Ferreira Pinto [29] classified as suitable the consolidants that are capable to penetrate more than 15 mm in depth.

According to Table 2, the amount of absorbed products was similar in 2hDGA and 2hTUDA, being slightly lower for 2hPEGBA. The dry residues obtained within the stone pores were similar to the ones obtained from the calcite blends, i.e. the 2hPEGBA showed significantly lower dry residue when compared to the xerogel counterparts, polymerized inside inert flasks.

The data corroborates our previous conclusions about the relevance of studying the products derived from sol-gel reactions under chemical environments comparable to the ones existing inside the stones pores [14].

Relatively to the consolidation efficacy (Fig. 6), the drilling profile of the stone treated with 2hDGA sol showed a quite uniform shape along the stone depth, without important heterogeneities (Fig. 6b). The force gain achieved was of around 2.3 N (6.5 N), which corresponds to a strength increase of 50 % in relation to the characteristic value of untreated stone. As already seen in the previous section, the 2hTUDA sol also produced a uniform strength gain, but the force increase was much more significant (gain of 100 %).

The distinct force gains are attributed to the different lengths of the PEG-CA chains. In fact, the small length of DGA "chain" could foresee a reduced outcome in enhancing the tendency to crack and the ductility of the silica network.

The results clearly highlighted the importance of the PEG-CA to act as flexible spacers on the silica backbone and their role on the initial efficacy.

According to the requirements concerning the efficacy of a treatment proposed by some authors, both sols, 2hDGA and 2hTUDA, can be considered to be applied: Delgado Rodrigues and Grossi [30] state that a consolidant should provide a drilling resistance gain of at least 25 %, while Sasse [28] report that the maximum of strengthening provided by a consolidant should be less than 3 times the mechanical resistance of the untreated and non-weathered stone.

Such intended strength improvements were achieved with quite low quantities of final residue within the stone pores (around 1 kg/cm^2) and presumably with a reduced influence on the porosity and fluid-transport properties of the original stone. It is important to notice that the final dry residue showed to be significantly less than the final dry residue obtained from a commercial product (2.5 kg/cm^2) [29]. Despite supplementary studies on these features are still required, the final residues suggest that excessive modifications that cause a loss of long-term stability due to incompatibilities with adjacent un-weathered stone are not expected.

The stone treated with 2hPEGBA showed a completely different drilling profile (Fig. 6b). A peak in the resistance was noticed near the stone surface. The maximum force obtained was five times the characteristic force of the untreated stone. However, the resistance gain becomes negligible in depths higher than 12 mm. As mentioned before, such heterogeneities have high potential of risk as they can accelerate degradation phenomena.

The major causes for this strong non-uniform drilling profile should not be the same as in the 10TUDA case. A concentration of species that are more able to provide resistance (PEGBA and highly pre-condensed siloxane species) remained in a more superficial zone, while smaller molecules (solvent, TEOS, and siloxanes with lower pre-condensation degrees) penetrated deeply into the stone pores (observed by capillary fringe rise).

Also, since the siloxane pre-condensation degree of this sol was lower than in other sols (due to the higher pH′), it was also more susceptible to be influenced by the alkaline media in depth, as proved by the poor cohesion provided to calcite powder (++) (see Table 2).

This distinct behavior was further investigated by analyzing the stone samples by SEM. The samples treated with 2hTUDA and 2hPEGBA were cracked perpendicularly to the stone surface and this cracking plane observed (at depth around 1–5 mm).

The calcite grains from the stone consolidated with 2hTUDA (Fig. 7a) were continuously covered by the consolidating material with a rough appearance. At the grains interfaces tendril-like structures bonding the grains were found. The consolidant accumulated at the contact points effectively bonded the grains between each others.

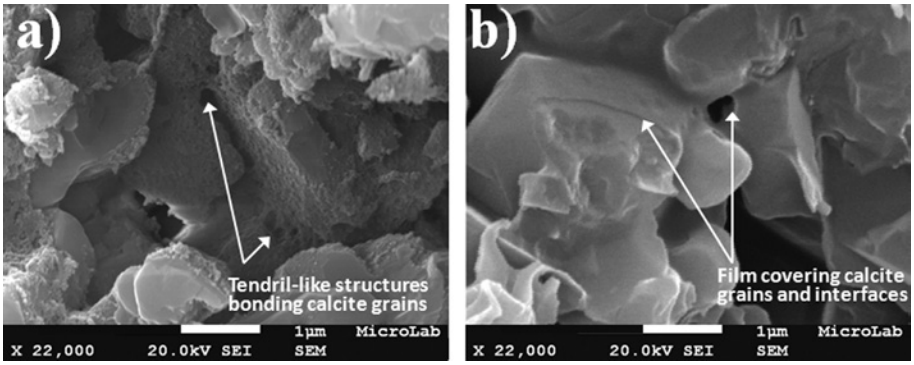

Fig. 7: SEM micrographs of the stones cracked surfaces treated with 2hTUDA (a) and 2hPEGBA (b).

The stone treated with 2hPEGBA showed a different appearance, the calcite grains were well-conformed by a continuous and smooth thin layer of consolidating material. The consolidating coating covered the grains and their interfaces, bonding the grains at the contact points. Both consolidants were well-conformed to the substrate exhibiting no shrinkage cracks and well-linked to it.

Furthermore, the differences between the Fig. 5c (which shows the stone surface treated with 2hTUDA) and Fig. 7a (showing a cracked surface of the stone treated with 2hTUDA) allows to distinguish different consolidating mechanisms. This indicates that in all cases there was some reverse migration to the surface. However, due to the uniform drilling profiles, such concentration at the surface seemed to have little relevance in the case of sols stirred for 2 h and 24 h.

This data emphasizes the importance of the selection of the surface to be analyzed by SEM when studying the mechanisms of consolidation and the overall appearance of the consolidating materials.

Conclusions

The modification of siloxane sols by introducing polyethylene glycol small chains end-capped with carboxylic acid groups is an efficient alternative to improve the initial efficacy of TEOS-based consolidants.

Despite being possible to produce xerogels with similar polymerization degrees and structures when the sol-gel reactions occurs within inert flasks, the efficacy of the treatment is dependent on the molecular weight of the chains when treating carbonate stones.

PEG-CA chains with higher molecular weights (like PEGBA) can cause non-uniform consolidations, while lower molecular weight chains (DGA and TUDA) can produce uniform and important strength gains in depth.

The use of PEG-CA in TEOS-based formulations produces consolidating materials that do not present shrinkage cracks that can conform and bond the calcite grains from limestones.

The treatment efficacy is, however, also highly dependent on the siloxanes pre-condensation degree. Since more sol-gel reactions are about to occur in the carbonate media for sols with lower pre-condensation degrees, these sols are more susceptible to reverse migration and, thus, non-uniform and poor strength gains in depth are achieved.

Any solution that cause a non-uniform consolidation, whatever the cause (lack of penetration, differential penetration, reverse migration, or inadequate polymerization path) can rarely be considered for application due to its latent harmfulness. Accordingly, the sols with higher potential of success are the 2hDGA and 2hTUDA.

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References

[1] M. J. Mosquera, J. Pozo, L. Esquivias. *J. Sol-Gel. Sci. Technol.* **26**, 1227 (2003).
[2] E. K. Kim, J. Won, J.-y. Do, S. D. Kim, Y. S. Kang. *J. Cult. Herit.* **10**, 214 (2009).
[3] S. Son, J. Won, J.-J. Kim, Y. D. Jang, Y. S. Kang, S. D. Kim. *ACS Appl. Mater. Interfaces* **1**, 393 (2009).
[4] J. P. Cardiano. *Appl. Polym. Sci.* **108**, 3380 (2008).
[5] C. Miliani, M. L. Velo-Simpson, G. W. Scherer. *J. Cult. Herit.* **8**, 1 (2007).
[6] C. Salazar-Hernández, M. J. P. Alquiza, P. Salgado, J. Cervantes. *Appl. Organomet. Chem.* **24**, 481 (2010).
[7] R. Zárraga, J. Cervantes, C. Salazar-Hernandez, G. Wheeler. *J. Cult. Herit.* **11**, 138 (2010).
[8] Y. Liu, J. Liu. *Constr. Build. Mater.* **122**, 90 (2016).
[9] D. Li, F. Xu, Z. Liu, J. Zhu, Q. Zhang, L. Shao. *Appl. Surf. Sci.* **266**, 368 (2013).
[10] J. F. Illescas, M. J. Mosquera. *J. Phys. Chem. C* **115**, 14624 (2011).
[11] J. Wen, G. L. Wilkes. *Chem. Mater.* **8**, 1667 (1996).
[12] M. J. Mosquera, D. M. de los Santos, T. Rivas. *Langmuir* **26**, 6737 (2010).
[13] M. J. Mosquera, D. Santos, T. Rivas, P. S. B. Sanmartín. *J. Nano. R.* **8**, 1 (2009).
[14] B. Sena da Fonseca, S. Picarra, A. P. Ferreira Pinto, M. F. Montemor. *New J. Chem.* **40**, 7493 (2016).
[15] B. K. Coltrain, S. M. Melpolder, J. M. Salva. In *Ultrastructure Processing of Advanced Materials*, D. R. Uhlmann, D. R. Ulrich (Eds.).DTIC Document, John Wiley & Sons Ltd, Chichester 69 (1992).
[16] G. Socrates. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, Wiley (2004).
[17] B. Chieng, N. Ibrahim, W. Yunus, M. Hussein. *Polymers* **6**, 93 (2014).
[18] D. L. Snavely, J. Dubsky. *J. Polym. Sci. A* **34**, 2575 (1996).
[19] R. Al-Oweini, H. El-Rassy. *J. Mol. Struct.* **919**, 140 (2009).
[20] C. J. Brinker, G. W. Scherer. *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*, Academic Press (1990).
[21] D. Costa, J. Delgado Rodrigues. "Consolidation of a porous limestone with nanolime", *12th International Congress on the Deterioration and Conservation of Stone,* New York (2012).
[22] C. Danehey, G. S. Wheeler, S. C. Su. The influence of quartz and calcite on the polymerization of methyl-trimetoxysilane, Seventh International Congress on the Deterioration and Conservation of Stone, Lisbon, 1043 (1992).
[23] C. Selwitz. *Epoxy Resins in Stone Conservation*, Getty Conservation Institute (1992).
[24] E. F. Hansen, R. Lowinger, E. Sadoff. *J.A.I.C.* **32**, 1 (1993).
[25] S. Rivers, N. Umney. *Conservation of Furniture*, Butterworth Heinemann (2003).
[26] G. Wheeler, G. C. Institute, *Alkoxysilanes and the Consolidation of Stone*, Getty Publications (2005).
[27] J. Delgado Rodrigues. "Consolidation of decayed stones". *A delicate problem with few practical solutions, Proc. Int. Seminar on Historical Construction*, Guimarães, 3 (2001).
[28] H. R. Sasse, Engineering aspects of monumental preservation. Restoration of Buildings and Monuments., **7**(2) (2001) 197–216.
[29] A. P. Ferreira Pinto. *Conservação de Pedras Carbonatadas*, Estudo e Selecção de Tratamentos., U.T.L., Lisboa (2002).
[30] J. Delgado Rodrigues, A. Grossi. *J. Cult. Herit.* **8**, 32 (2007).