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An Evaluation of Ethyl Silicate-Based
Grouts for Weathered Silicate Stones

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Arts
in Conservation of Archaeological and Ethnographic Materials

by

Brittany Helen Dolph

2014

ABSTRACT OF THE THESIS

An Evaluation of Ethyl Silicate-Based
Grouts for Weathered Silicate Stones

By

Brittany Helen Dolph

Master of Arts in Conservation of
Archaeological and Ethnographic Materials
University of California, Los Angeles, 2014
Professor Christian Fischer, Chair

Culturally significant monuments made of weathered siliceous stone often display sub-surface condition issues such as cracks and voids. These issues require grouts that are ideally compatible with the composition and properties of the substrate. Based on the successful application of ethyl silicates as consolidants in recent literature, this study examines possible formulation pathways for the development of a grout incorporating ethyl silicate. Tetraethylorthosilicate (TEOS), dibutyltin dilaurate (DBTL) as a catalyst, silicone oil (PDMS), various grades of ground quartz, sepiolite, and hollow glass spheres were used in differing concentrations to create samples. These were visually and physically assessed on workability, separation, shrinkage, cracking, strength, and

flexibility. Quantitative analysis was performed on selected formulations using UV-Vis-NIR reflectance spectroscopy in coordination with a weight loss experiment to investigate kinetics, dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). Successful formulations tended to include oligomeric TEOS, crushed quartz of mixed grades, sepiolite powder, and PDMS, and show promise for future investigations.

The thesis of Brittany Helen Dolph is approved.

Ioanna Kakoulli

Gaurav Sant

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University of California, Los Angeles

2014

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1. Introduction

Stone has been used both as a building material and a medium for figurative and abstract artistic expression for millennia. While its selection by a society was often determined by the local availability of raw materials (rocks), a particular type may also have been chosen based on its inherent workability, strength and/or aspect. These properties, in turn, are primarily determined by the mineralogical composition, texture, structure and porosity of the stone. Paradoxically, the vulnerability of the stone to deterioration will also partly depend on these intrinsic characteristics as well as on the influence of external factors mainly related to environmental and climatic conditions.

Among all external factors, water can be considered the main deterioration agent. Soluble salts that can originate from the environment, the stone itself and/or biological activity, are transferred into and through the porous network of the stone by the movement of liquid water. Upon evaporation, these salts can precipitate either on or near the surface as well as deeper into the material, depending on the state of a complex balance between capillary forces, evaporation gradients and salt solubility. The crystallization pressure created by the precipitation of a salt from a supersaturated solution places physical stress on the fabric of the stone and can cause severe damage. Moreover, if the salt is deliquescent, the damage can be amplified by cycles of crystallization and dissolution controlled by changes in temperature and/or relative humidity.

Changing temperatures can also cause thermal dilation and contraction of the stone, as can the freezing and thawing of water, all of which induce differential mechanical stress on the surface and inside the stone material. The force of wind

carrying small particulate and/or the impact of rain can contribute to surface erosion. In addition, rain can also partially dissolve some both minerals and unstable glassy phases in the stone, leading to the formation of sub-surface voids. This is especially true when the rain is acidic, which can be particularly detrimental for limestone. Finally, the development of biological activity can further contribute to chemical and mechanical decay.

Although not exhaustive, the above description clearly shows that the combination of the intrinsic properties of the stone and the external factors determines the type, extent and rate of decay. Degradation then occurs in a multitude of forms such as granular disintegration, efflorescence, flaking, spalling, microcracking to name only a few.

Historically, stone consolidants have been employed to address superficial condition issues in an effort to both restore cohesion between mineral particles and strengthen the weathered surface of the stone, but deeper condition anomalies such as cracks and sub-surface voids have altogether different requirements. For the latter, conservation interventions typically consist of the injection of a material, otherwise known as a grout, that fills the empty space and adheres to the stone on either side. Grouts must have enough consistency to fill voids and the necessary fluidity to be applied with a syringe, while introducing sufficient cohesion to stabilize the crack without forming a bond that is stronger than the stone itself. As with all conservation interventions, bonds introduced to an object must not be stronger than the substrate, ensuring that any applied stress will break the bond before the substrate.

Furthermore, a major guiding conservation principle is that applied conservation materials, including consolidants and grouts, should match as closely as possible the composition and properties of the substrate material, as similarity is likely to result in fewer adverse interactions. For example, it is generally recognized now that inorganic consolidants are more appropriate for inorganic substrates, especially in harsh outdoor environments where organic-based consolidants may degrade at a much faster rate than the object they are intended to protect. For this and other reasons, ethyl silicates have been widely used for the consolidation of stone, often with better results on silicate-based stones than on calcareous ones.

On the other hand, commercial grouts are almost exclusively lime- and cement-based products. Though they have been used on all types of stone, lime- and cement-based products might be more appropriate for calcareous stones, such as limestone and marble. Along this line of reasoning, ethyl silicate-based grouts might be better adapted to silicate-based stone, but very few accounts on the use of such grouts have been published.

This thesis explores formulation pathways for the development of a grout with ethyl silicate as the main component. In order to achieve the expected properties, various fillers and additives were selected for testing. These materials were chosen based on their intrinsic characteristics that could potentially improve the final properties of the grout while still providing adequate workability. Building upon the large body of research on ethyl silicate-based consolidants, various formulation options were evaluated. Particular focus was placed on modifications of the sol-gel transformation of

ethyl silicate induced by the presence of other components (fillers, additives) at various concentrations.

Ultimately, the objective of the research presented here is to provide some basic understanding and useful guidelines that could help to develop ethyl silicate-based grouts for the treatment of lacunae, subsurface voids, and cracks in porous stones of relatively low cohesion. A review of relevant work on ethyl silicate and its role in stone consolidation and grouting follows, as does a description of the materials used and quantitative and qualitative modes of investigation employed, and finally a discussion of the results.

2. Background and Literature Review

2.1. Stone Consolidation

A good operable definition for consolidant is a material that “acts at the near-molecular level by fixing or inhibiting the capacity for movement between very small particles, thereby altering the characteristics of the material in terms of its behavior, particularly in the presence of water. It tends to make the material stronger in compression and tension, and may affect inherent characteristics such as heat and sound transmission and rigidity” (Warren 1999) (Fig.1). Conservators typically select consolidants to address flaking, spalling, powdering, delamination, and other types of surface condition issues resulting from low surface cohesion. The ideal consolidant, however, just like any applied conservation material, must possess a complex web of aesthetic, chemical, physical, and working properties, not least of which include durability over time and ease of application. It must retain sufficient mechanical strength

and adequately improve cohesion, while changing the final color or gloss of stone as little as possible, nor can it introduce damaging byproducts such as salts. Ultimately, it must not alter the water transfer properties of the stone either, so as to shift the buildup of moisture from rising damp, precipitation, or humidity. A number of approaches attempting to fulfill these criteria have relied on materials ranging from inorganic lime-based treatments to organic compounds such as epoxy and acrylic resins (Doehne and Price 2011). Ethyl silicates provide yet another alternative that has met some success, especially when applied on silicate-based stone such as sandstone. Advantages include stability when exposed to light over time, bond strength, and low viscosity (and thus ease of penetration), all of which make ethyl silicates a good option (Wheeler 2005).

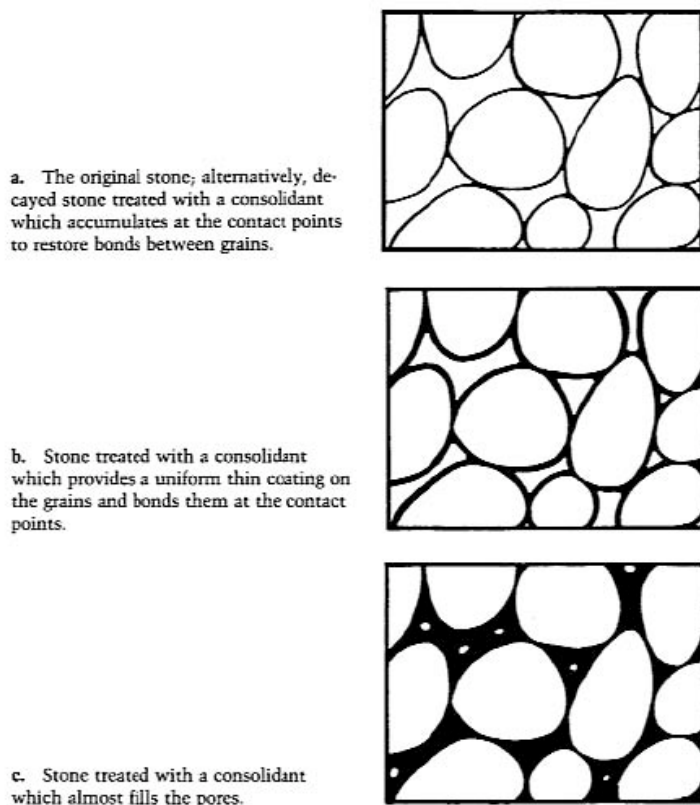


Fig. 1: Schematic showing stone consolidation (Clifton 1980)

2.2. Ethyl Silicate: Chemistry and Processes

Ethyl silicate, often referred to as tetraethoxysilane or TEOS is a tetrafunctional silicon alkoxide (Fig. 2) synthesized by reacting ethanol with silicon tetrachloride (SiCl_4). The transformation of ethyl silicate into a silicate gel occurs upon reaction with water through a sol-gel process where components are mixed into solution, then undergo hydrolysis and condensation reactions to form an inorganic gel network. At the functional group level, the sol-gel process can be schematically described with the two following reactions:

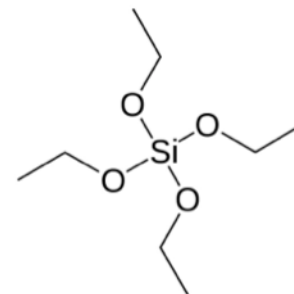
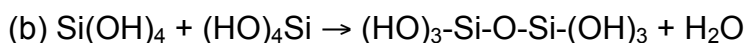
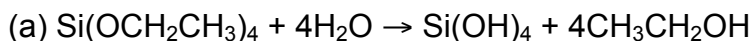


Fig. 2: Chemical structure of TEOS



The hydrolysis reaction (a) replaces the ethoxy groups with hydroxyl groups, which subsequently form siloxane bonds (Si-O-Si) through a condensation reaction (b). The latter can also occur between ethoxy and hydroxyl groups (alcoholysis) and in all instances, ethanol is released during the process. The hydrolysis and condensation reactions of TEOS are usually catalyzed with acids or bases, and alcohol is also often added as a co-solvent in the initial mixture because water and TEOS are immiscible (Brinker and Scherer 1990). From a structural point of view, the first molecules of silicic acid will react together to form a sol composed of silica nanoparticles suspended in the reactants mixture, which will further react to produce the final silicate gel (Fig. 3).

The initial water:TEOS ratio as well as the type and amount of catalyst and co-solvent determine the rate and extent of hydrolysis, but also the nature of the final gel (Wheeler 2005). Depending on the sol-gel synthesis methodology and drying conditions, a variety of final products such as bulk gels, films, fibers, powders (xerogels, and aerogels) or monodispersed particles (Stöber silica) can be obtained (Brinker and Scherer 1990, Jones 2012).

For stone consolidation, on the other hand, TEOS is typically used pure or slightly diluted in an organic solvent. The rate of the hydrolysis and condensation reactions are primarily controlled by the relative humidity and the amount of water in the stone itself. In order to avoid stability issues due to acidic or alkaline conditions, commercial TEOS-based consolidants often contain an organo-metallic catalyst such as dibutyltin dilaurate (DBTL).

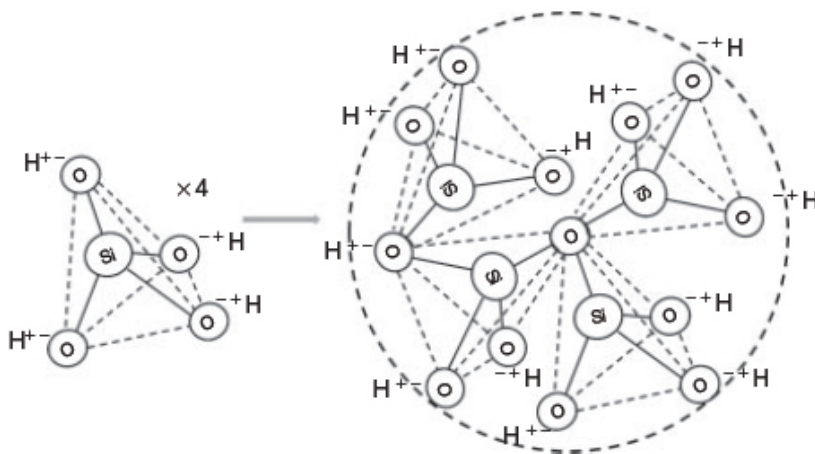


Fig. 3: A schematic representation of silica tetrahedra (silicic acid) forming a nanoparticle in a sol (Jones 2012)

2.2.1. Ethyl Silicates for Stone Consolidation

Ethyl silicates have been the most widely used stone consolidants for the past forty years, often with better results on sandstone and other silicate-based stones than on limestone and marble (Scherer and Wheeler, 2009; Doehne and Price, 2011).

Comparisons of ethyl silicate consolidants applied on sandstone and limestone using scanning electron microscopy (SEM) have shown differences in the interactions with the substrate, whereby the ethyl silicates did not conform or link to the calcite grains in the limestone while providing adequate improvement in cohesion on sandstone (Charola and Koestler 1986; De Witte, Charola, and Sherryl 1985). This is in part due to the fact that, while ethyl silicates can develop a physical bond with the substrate by penetrating a porous and irregular surface, chemical bonds can only form when hydroxyl groups are available on the surface of the mineral phases to condense with the silanols produced during the hydrolysis of ethyl silicate (Scherer and Wheeler 2009). On the other hand, the use of the ethyl silicate (Conservare OH) to consolidate fragments of an archaeological lime plaster statue were judged successful when both strength and morphological homogeneity were maintained over 11 years, though the authors suggest that this may be in part due to the much finer particle size of the marlaceous lime plaster as compared to the calcite of limestone, on which much prior research had taken place (Grissom 1994). In this case then, the research suggests that the mechanical adhesion was sufficient to provide strength and stability to the lime plaster surface.

However, when applied to porous silica-rich stone such as sandstone or volcanic tuff, consolidation treatments with ethyl silicate have been shown to significantly

improve the mechanical properties, increasing the compressive strength of the surface anywhere from 66 to 296%, depending on exposure time and dilution (Wheeler 2005; Laurenzi Tabasso et al. 1994; Useche 1994; Goins 1995).

Yet, ethyl silicate-based consolidants still have drawbacks, the most critical being the tendency to shrink during the formation and drying of the gel. As the gel coarsens, it develops an increasingly low Young's modulus and becomes brittle, which results in the formation of cracks as intense capillary pressure is exerted on the network (Fig. 4). Efforts to counteract shrinkage have led to the development of particle-modified consolidants (PMCs). The addition of colloidal oxide particles with a diameter of 0.5 – 2 μm to TEOS has been shown to enlarge the pore size within the network and increase the modulus, which in turn reduces shrinkage as a result of lower capillary pressure (Escalante, Valenza, and Scherer 2000).

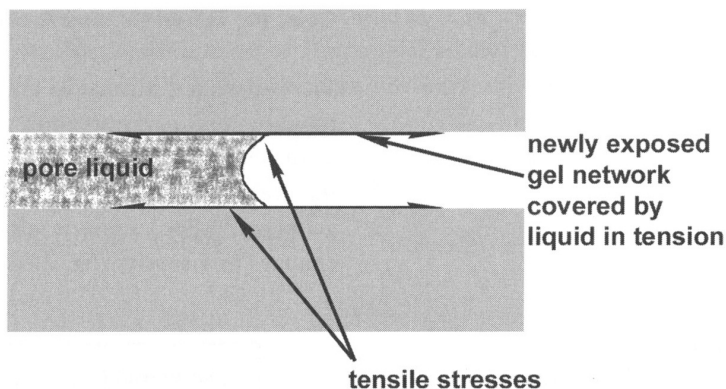


Fig. 4: Tensile stresses created by the stretching pore liquid during drying (after Brinker and Scherer 1990). As the gel begins to dry, pore liquid stretches out to cover the exposed solid gel network (Wheeler 2005)

However, the particles often form agglomerates, increasing the overall viscosity and thus reducing the penetration potential of the sol, which might result in pore blockage. The properties of the final gel can be modified while preventing excessive agglomeration by adsorbing nanoparticles onto the oxide particles (Miliani, Velo-

Simpson, and Scherer 2007; Aggelakopoulou et al. 2002). On the other hand, PMCs do present aesthetic issues for a surface consolidant as the larger pore size creates a gel that lacks transparency, contributing to a “noticeable whiteness” (Miliani, Velo-Simpson, and Scherer 2007). Smaller particles also increase the likelihood of particle agglomeration, which requires particle surface modification to prevent, or vigorous agitation to break up once in solution. Slightly larger particle sizes may be utilized to avoid this degree of agglomeration; however, larger particles may have a greater tendency to settle, causing separation.

Another solution to minimize shrinkage and cracking problems is based on the addition of polydimethylsiloxane to the TEOS to create flexible bridges within the network (Fig. 5). Alternatively called organically modified silicates (ORMOSILS), these inorganic-organic hybrids allow the sol to maintain a lower viscosity and higher penetration into stone matrices, while incorporating flexibility into the final gel to withstand cracking. The organic components can be chemically bonded to the silica matrix, impregnated into the porous oxide gel, or simply trapped in the silica gel matrix. The addition of hydroxyl-terminated polydimethylsiloxane (PDMS-OH), which chemically bonds with the silica, can produce a composite that is harder than a pure PDMS-OH based network and more flexible than the silica gel alone (Mackenzie and Bescher 1998). More recently, it has been shown that the addition of short PDMS-OH chains (5%) to TEOS catalyzed with DBTL effectively diminished cracking in the TEOS matrix (Zárraga et al. 2010).

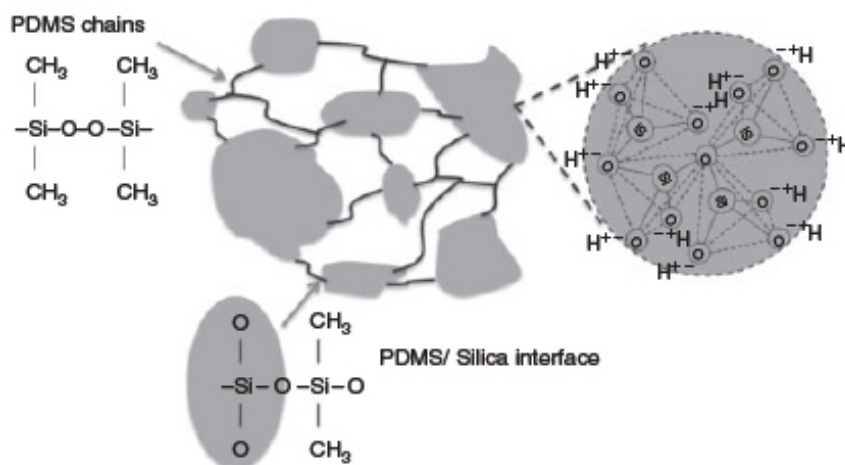


Fig. 5: Schematic showing the nanostructure of Ormosils. Inset shows an example of the silica network (Shirosaki et al. 2012)

Other particle types may be employed to reduce shrinkage and improve flexibility of silica gels based on polymer composites research, in particular on the reinforcement of silicone elastomers with sepiolite (Bokobza, 2004). The capacity of these additives to effectively reinforce the final gel depends on the particle size, particle shape, and degree of dispersion within the sol as well as on the interactions with the matrix material, and sepiolite with its form factor and molecular structure (Fig. 6) is potentially a good candidate.

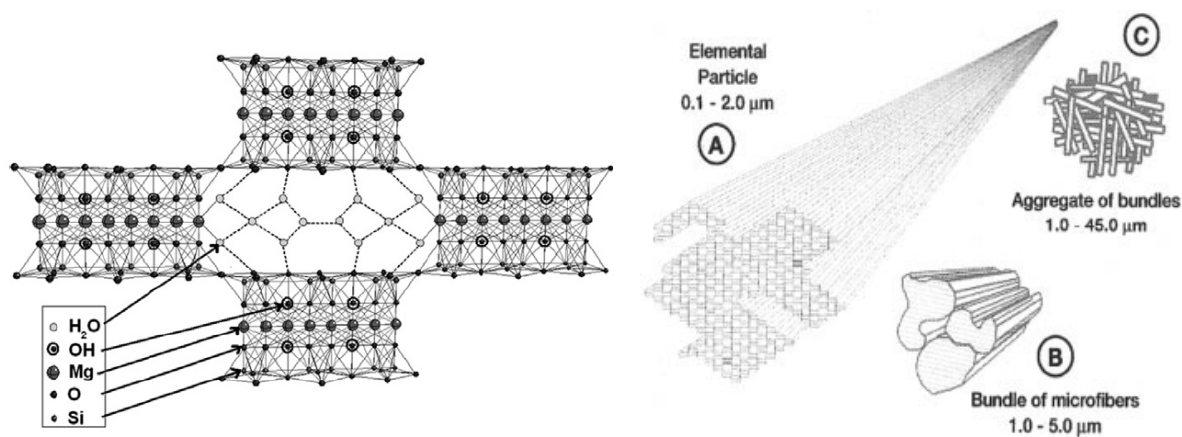


Fig. 6: Crystalline structure (left) and micromorphology of sepiolite (right); from Tartaglione 2008 and Bokobza 2004.

Recently, Li et al. (2013) showed that a silica aerogel prepared from TEOS and reinforced with organically-modified sepiolite had improved mechanical properties over the neat silica aerogel, such that the compressive strength increased with an increased sepiolite composition. Furthermore, the sepiolite-reinforced silica aerogel showed reduced shrinkage as the concentration of sepiolite was increased from 0 to 1.5%, due to the strengthening effect that allowed the gel to withstand the forces imposed during the drying stage. The sepiolite fibers were demonstrated to be well-dispersed within and displayed reactivity with the surrounding silica matrix. These results are promising in spite of the fact that the reactions progressed under supercritical drying conditions and may have led to different results in ambient ones.

2.3. Grouts

An ideal grout shares some properties with a consolidant, including durability over time, provision of mechanical strength appropriately matched to the substrate, ability to increase cohesion, and preservation of aesthetic and water transfer characteristics, while not introducing harmful byproducts. With a view to these shared desired properties, ethyl silicates were selected as a base on which to build the grout formulations for this thesis.

However, grouts differ in a few key aspects from consolidants: they must be of enough low viscosity to be injectable and yet provide the necessary consistency to take up the small but open spaces of cracks and subsurface voids as they set and dry (Fig. 7). In addition, the material should have similar mechanical properties to the substrate, including thermal expansion coefficient and flexibility, to allow for natural movement of the substrate without failure.

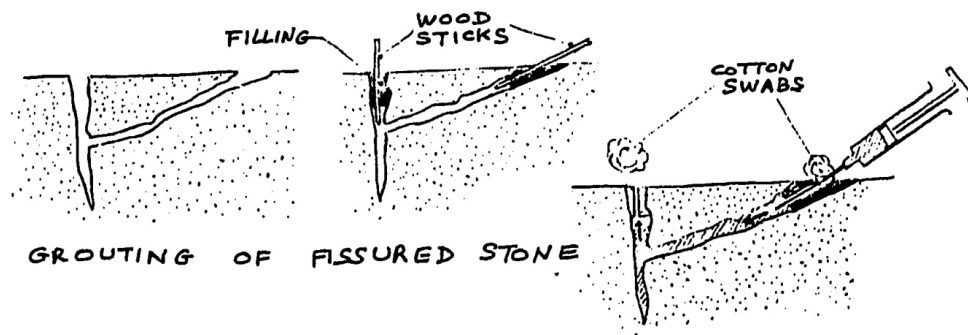


Fig. 7: Schematic showing clearing of particulate from fissures in stone, followed by grout injection (Torraca in Lazzarini & Piper 1998)

Most grouts used in the field of stone conservation are lime-based grouts. These materials have a long history, having been documented as far back as ancient Rome and used in masonry construction of walls, bridges, and aqueducts (Houlsby 1990). Grouts most likely developed from lime mortar, a material with much more consistency composed of lime and various aggregates mixed with water and also valued for its structural adhesive properties. Conversely, lime-based grouts usually do not contain aggregates and have a lower viscosity and higher flow in order to be applied by injection.

Unreacted alkoxysilanes such as TEOS are liquids of low viscosity, an important property when applied for consolidation purposes as it enables effective penetration into the porous network of the material to be treated. On the other hand, to formulate an ethyl silicate-based grout, bulking agents or fillers must actually be added in order to increase the consistency and reduce the flow so that the material will not be absorbed so easily by the porous stone, remaining instead in place to fill the larger voids.

2.3.1. Ethyl Silicate-based Grouts

While lime-based grouts have been addressed much more thoroughly in the conservation literature than ethyl silicate grouts (Pingarrón Alvarez 2006; Wong 2006; Chaudhry 2007; Kalagri et al. 2010), application tests were performed on grout formulations that included ethyl silicate grouts for the conservation of the Lausanne Cathedral built with Molasse sandstone (Rousset et al., 2005). Various lime, ethyl silicate, and hydraulic grouts were prepared and evaluated based on viscosity, injectability, setting time, shrinkage, and adhesion. The ethyl-silicate grouts included a formulation with a mixture of oligomeric and monomeric TEOS (Funcosil 500STE and 300E from Remmers, Germany) blended with quartz powder, hollow glass spheres, and pigment fillers. The second ethyl silicate formulation consisted of Syton X30 mixed with hollow glass spheres, molasse powder, and fumed silica. Comparisons ranked the lime-based grouts preferable on qualitative performance, but this was in part due to the fact that the ethyl silicate grouts were not applied as films within the critical maximum thickness of 5 mm. Good adhesive properties were also acknowledged for the ethyl silicate formulations, in spite of their propensity for shrinkage and crack formation in voids larger than the critical thickness. In comparison to the lime-based grouts devoid of any shrinkage and cracks, the Funcosil grouts showed a few cracks and shrinkage, which were even more pronounced for the Syton grout. However, the Funcosil formulations received a rating of “very good” for viscosity, injectability, and setting time, and the Syton a rating of “very good” for injectability, and “good” for viscosity and setting time. Overall, the ethyl silicate grouts performed the best in working properties (Rousset et al. 2005). These results suggest the good potential for successful application of an

ethyl-silicate grout, if the shrinkage and cracking issues can be mitigated to some extent.

Another study involved an investigation of ethyl silicate grouts originally formulated for the conservation of the Angkor Wat sandstone temple, which were applied to various types of American sandstone samples. The formulations tested three different commercial ethyl silicates: the Funcosil 500STE and 300E, and an ethyl polysilicate (Silbond 50), both of which were mixed with a fine silica powder (63–75 μm). Various mechanical properties of the gel and water transfer properties of the stone were measured after treatment in the laboratory with overall inconsistent results and often specific to the sandstones on which they were tested (McIntosh 2007). The author also notes that while ethyl-silicate grouts have been used worldwide on sandstone substrates, very few evaluations of these applications appear in the literature.

2.4. Field Conservation

In addition to the typical testing carried out on conservation materials prior to application, materials that will be applied in the field, such as on outdoor sculptures and architectural elements, need to fulfill even more requirements. Field conservation imposes numerous limitations on the methodology and materials utilized during a conservation intervention. The absence of laboratory facilities means that materials must be easy to prepare, with instruments and tools that are portable. In the case of grouts, formulations must either be simple to prepare in small quantities, or have a long enough shelf life so that larger amounts can be prepared ahead of time and remain stable. Relative humidity and temperature can also affect the rate of chemical reactions such that a given product should have the ability to be modified for a wide range of

environmental conditions, or at least over a range appropriate for the climate in question. Application methods and testing of materials in the laboratory should integrate this variability as much as possible. Once in the field, choosing the appropriate methodology and the best time of the day for the application is often a key for a successful treatment (Fig. 8).



Fig. 8: Photo of author injecting grout into fissures in weathered sandstone seats in the field at the Theatre of Demetrias, Volos, Magnisia, Greece (Courtesy of Hara Topa, 2012)

3. Materials

3.1. Ethyl Silicate

Two types of ethyl silicate supplied by the company Evonik (Degussa) were used in this research: Dynasylan® A and Dynasylan® 40. Both are based on tetraethyl

silicate (TEOS), which is a clear, colorless liquid of low viscosity with a faint ester-like odor.

Dynasylan® A is mainly composed of TEOS monomers (98%, silicon dioxide content of 28.5%) that upon reaction with water vapor forms a hydrated silica gel (SiO_2). Dynasylan® A is most often applied as a coating on inorganic substrates to improve chemical and thermal stability and mechanical properties. Monomeric TEOS is also used for the synthesis of silica and silica gels for industrial and research purposes.

Dynasylan® 40, unlike Dynasylan® A, is an oligomeric ethyl silicate composed of pre-polymerized TEOS (85-90%) and TEOS monomers (10-15%) with a silicon dioxide content of about 41% upon complete hydrolysis and condensation. Due to their linear structure, the short chains impart a degree of flexibility to the gel as it hardens, rather than promoting the rigid cross-linked network that the monomers would form. Dynasylan® 40 is used as a paint binder, a crosslinker for coatings, and for sol-gel processes, often in combination with other functionalized silanes and organic components to create a silica gel matrix with modified properties (Appendix B).

Both Dynasylan® A and 40 are immiscible with water without a co-solvent though small amounts of water are required for hydrolysis to proceed.

3.2. Dynasylan® AMEO and GLYMO

AMEO (or 3-aminopropyltriethoxysilane) is an ethoxysilane that also contains a primary amino group. The additional functionality offered by the amino group may be used in applications to promote adhesion, act as a coupling agent for organic substrates, to modify surface properties, and as a cross-linking agent. AMEO is a liquid at ambient conditions, with a color ranging from colorless to pale yellow, and an amine-

like odor. GLYMO (or 3-Glycidyloxypropyltrimethoxysilane) is a methoxysilane that contains an epoxy group. Like AMEO, GLYMO can be used as an adhesion promoter, a coupling agent, and a cross-linking agent. It is a colorless liquid with little odor.

All Dynasylan® products should be stored in tightly sealed containers as excess ambient water vapor allows hydrolysis to proceed. Hydrolysis of alkoxysilanes also results in the release of volatile organic compounds (VOCs) in the form of ethanol, and its use is consequently restricted by many state legislations.

3.3. Catalyst

Di-n-butyldilauryltin (Fig. 9) or dibutyltin dilaurate (DBTL) was obtained from Gelest, Inc., and is a translucent pale yellow liquid with a characteristic odor. DBTL is primarily used as a catalyst for the polymerization of polyurethanes and silicone-based compounds. For TEOS, DBTL promotes the condensation of the silanol groups formed

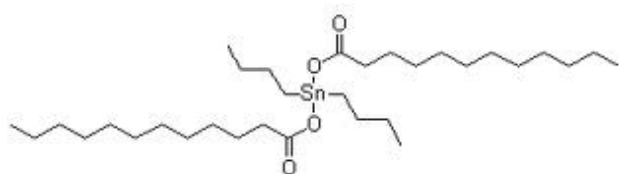


Fig. 9: Chemical structure for Dibutyltin dilaurate

after hydrolysis reactions and is present in a number of commercial TEOS-based consolidants, such as SILRES® BS-OH-100 (Wacker, Germany) marketed in the

United States as Conservare OH100 (Prosoco, Inc.).

3.4. Silicone Oil

A silanol-terminated polydimethylsiloxane (PDMS-OH)¹ with reference DMS-S12 (Gelest, Inc.) was used for this research. This silicone oil is composed of short polymer chains with a molecular weight of about 400 to 700 g/mole corresponding to 'n' values comprised between 5 and 10 (Fig. 10). It is a clear and colorless liquid with a low viscosity (20-35 cSt). Beside the advantage of the reactivity introduced by the silanol groups, it should be mentioned that the presence of the methyl groups imparts also some hydrophobic properties to the chains that can result in poor adhesive qualities.

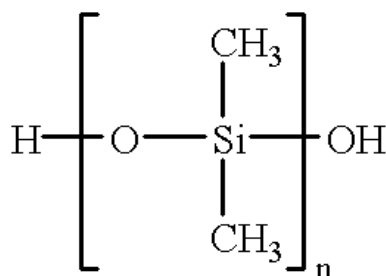


Fig. 10: Chemical structure of a hydroxyl-terminated PDMS

¹ Being the only silicone oil used in this study, it will be simply referred to as PDMS

3.5. Fillers

Ground silica and sand fillers were provided by U.S. Silica Company. Several grades of silica with the following references: Min-u-sil® 5 (M5), 15 (M15), 40 (M40) and Sil-co-sil® 75 (Sil-75) as well as a ground sand (GS-40) were used for the formulations. Available data about particle size distribution are given in Table 1. Filler samples were used as received, but stored in tightly closed containers to avoid additional adsorption of water vapour. This was particularly important for the finest grade (M5), which has a higher specific surface and had a tendency to form aggregates.

Table 1: Particle size characteristics for the ground silica and sand fillers		
Ground Silica	Median Ø (µm)	% < (X µm)
Min-u-sil 5	1.4	97 (5 µm)
Min-u-sil 15	4.1	98 (15 µm)
Min-u-sil 40	8.7	98 (40 µm)
Sil-co-sil 75		98 (75 µm)
GS-40	~ 300	99 (600 µm)

Hollow glass microspheres (HGS), which appear as a low density fine white free-flowing powder composed of thin-walled glass spheres, were supplied by Trelleborg Offshore US, Inc. The SID-200Z grade (Eccospheres®) was chosen and is characterized by a mean particle size of 53 µm and a true particle density of 0.20 g/cc. The spheres retain a high strength, with a collapse pressure of 1000 psi, ensuring robustness during mixing. The surface of the microspheres is also treated with an epoxy-functionalized silane to promote interfacial bonding.

3.6. Sepiolite

Two types of sepiolite were used in this study, manufactured and sold by Tolsa S.A. (Spain) under the tradename Pangel®. Both are organically modified micronized

sepiolites, Pangel B5 contains >80% sepiolite and <20% quaternary ammonium compounds and benzyl-C₁₄-C₁₈-alkyldimethyl chlorides; for Pangel B10, these percentages are >85% and <15%. The organic treatment of the sepiolite increases the compatibility with solvents and compounds of low (B5) and low-to-intermediate polarity (B10). It is designed to provide thixotropic and suspension properties to formulations and is often used to thicken greases, oils, and drilling mud.

4. Experimental Procedures

Six sets of trials, each with multiple formulations, were carried out in an effort to explore the effects of the various components, formulation parameters and experimental conditions as follows: the presence and concentration of each component, the effect of the solid-to-liquid ratio, the effect of order in which components were added to the bulk mixture, and the influence of relative humidity. Workability and separation of the solid-liquid mixtures, as well as shrinkage, cracking, strength and flexibility of the gel were evaluated visually and qualitatively.

4.1. Sample Preparation

The TEOS products, Dynasylan® A (DA) and Dynasylan® 40 (D40), were catalyzed with 1% of DBTL and in the remaining of this thesis, the terms TEOS, D40 or DA will refer to ethyl silicate with added catalyst. Test formulations were created using a solid-to-liquid ratio of either 3:2 or 1:1, based on data in the literature (Rousset, 2005). Solids included ground quartz, sand, sepiolite, and hollow glass spheres, while the liquid components besides TEOS included GLYMO or AMEO, and PDMS-OH. In

general, liquids were added to the solids; however, for some of the more complex formulations, variations in the addition order of the components were tested, though not systematically. For each trial, small amounts were prepared (15-30 g) and mixed by hand until visual uniformity was achieved. After having been thoroughly mixed, formulations were poured into glass petri dishes. Both glass dishes ($\varnothing$ 60 mm, H. 15 mm) and lids were used, the latter resulting in a slightly thinner film as the amount of added material was kept constant.

Petri dishes were placed in a large plastic box containing a pan filled with a supersaturated solution of sodium chloride, which allowed for maintenance of the relative humidity around 75%. The solution was occasionally stirred when the salt began to creep on the sides of the plastic pan. Trials were kept in the container for at least 7 days though briefly taken out from time to time for photographs and observations.

Both Set 6 and the reference trials were also evaluated in conditions of low relative humidity (6-D). Trials were placed in a tightly sealed chamber with enough silica gel to keep the RH between 20 and 30%. In addition, the reference trials and the ones of set 6 were used to study the kinetics of the sol-gel process and were taken out and weighted at regular intervals. Some trials (set 6) were also analyzed with UV-Vis-NIR spectroscopy during the weight loss experiment.

The reference trial set included a group of 4 trials in glass dishes ($\varnothing$ 100 mm, H. 20 and 15 mm). The volume was calculated in order to achieve a thickness of 2 mm, to test whether limiting the dimensions might impart less stress unto the bulk material, and thus result in less cracking. The container with the reference trials was loosely covered, but left to react in ambient conditions.

Some formulations were prepared on large glass plates in order to obtain a film for Dynamic Mechanical Analysis (DMA). Thickness was controlled by placing two strips of a 2 mm-thick plexiglass sheet onto the glass plate; once the material was poured onto the glass, another piece of Plexiglas was used to spread it out to obtain a film with a smooth surface. Plexiglass strips were removed shortly thereafter (Fig. 11). The resulting films, as well as other samples from dishes, were sawed and sanded to size for DMA, which required samples approximately 1 mm in thickness, and at least 5mm wide.



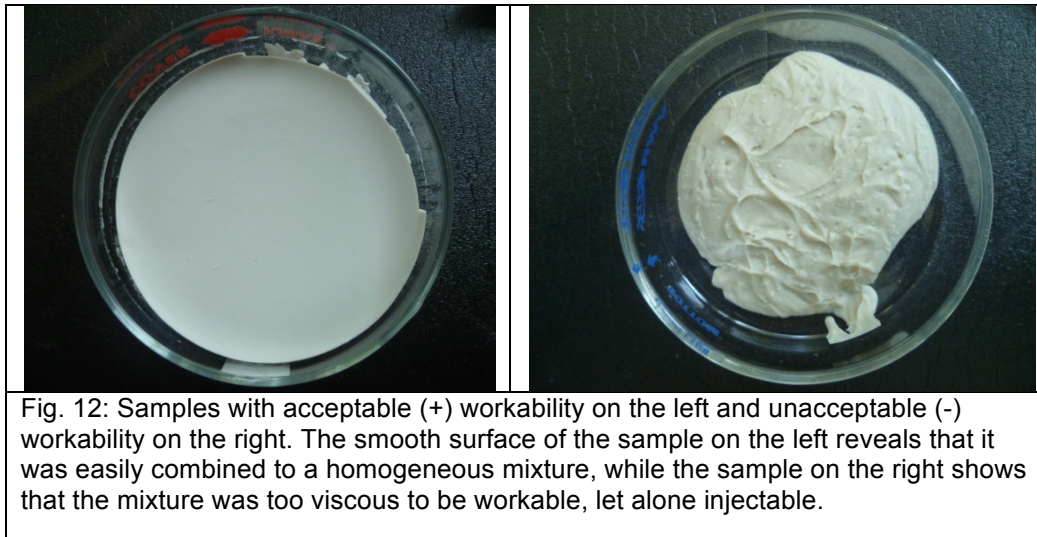
Fig. 11: Aspect of the film after removal of the Plexiglas stripes from the glass plate

4.2. Evaluation Methodology

4.2.1. Qualitative Tests

All of the trials were qualitatively assessed and only those that produced the most promising results were selected for further analysis. The qualitative tests primarily consisted of the evaluation of the following properties: workability, separation, shrinkage, cracking, strength and flexibility.

Workability was assessed simply on the basis of whether the formulation could be mixed, and subsequently poured into a dish (Fig. 12). Those that retained enough flow to be mixed and poured received a positive rating (+), while those that had to be spread or did not flow into the dish were given a negative rating (-).



Separation was evaluated with a similar rating system. Formulations that showed no separation received two plusses (++), minor or partial separation received one plus (+), and those that showed clearly visible separation throughout the bulk receive a negative (-) (Fig. 13).



Fig.13: Samples showing no separation (++), minor separation (+), and clearly visible separation (-). Separation is evident where particulate has sunk to the bottom of the dish, leaving the transparent, glassy surface of the silica at the top, and resulting in crizzling and sometimes peeling of the top layer. The center sample shows partial separation at the right side of the dish, where minor crizzling has occurred in a localized area.

For shrinkage, two plusses (++) denotes that there was very little space between the sample and the edges of the glass dish, one plus (+) showed a moderate amount of space between the sample and the glass, or between the fragments, and a negative (-) represented very obvious and large gaps between the sample and the glass or fragments (Fig. 14). However, warping and a large extent of bulk cracking were also considered as indications of shrinkage.

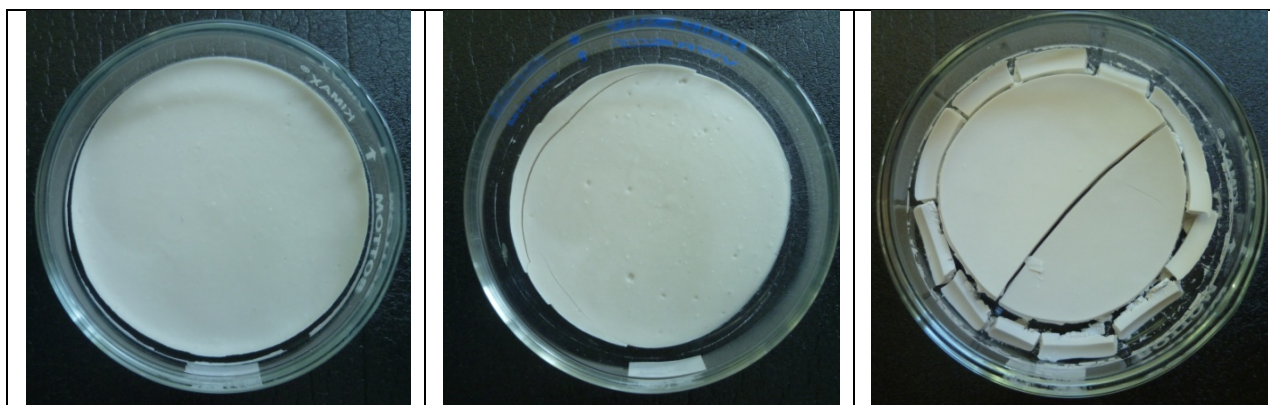
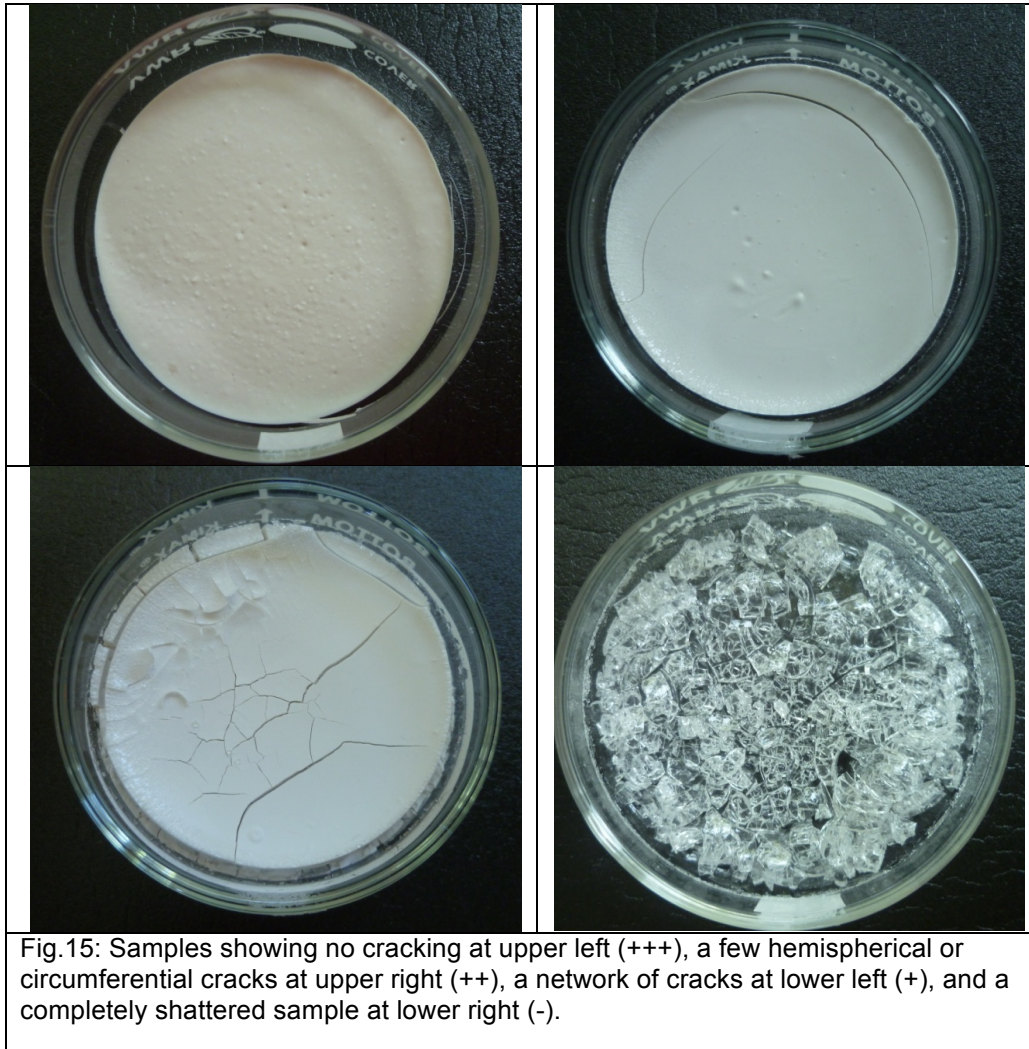


Fig.14: Samples showing very little to no shrinkage (++), moderate shrinkage (+), and much shrinkage (-) based on gap between the material and the glass dish.

The assessment of cracking was based on the visible extent of cracks through either one layer if separation had occurred, or through the bulk material. Three plusses

(+++)¹ represented no cracks at all, two plusses (++) were assigned to samples showing a few cracks or hemispheric or circumferential cracking only, one plus (+) meant a network of cracks in addition to hemispheric and circumferential cracking, and a negative (-) meant that the sample was completely shattered, with an extensive network of cracks and microcracks (Fig. 15).



Strength and flexibility were also scaled on a range from three plusses (+++) for the most strong or flexible respectively, with a negative (-) rating for weak or brittle samples.

4.2.2. Quantitative Tests

Quantitative analysis included the weighing and performance of Ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy on the samples over time in order to identify the components present and assess the progress of the reactions, DMA to measure the mechanical properties of the final gel product, and scanning electron microscopy (SEM) to evaluate the morphology and microstructure of the final gel product. Each of these methods is described in further detail below.

UV-Vis-NIR spectroscopy is a technique that allows investigation of the characteristics of a material based on its spectral signature. For this research, UV-Vis-NIR spectroscopy was used in an attempt to monitor the intensity of specific functional groups, and thus follow the hydrolysis and condensation reactions during the sol-gel process. Measurements were carried out using an ASD Inc. Fieldspec® 3 spectrometer covering a spectral range from 350 to 2500 nm and equipped with a high intensity contact probe (spot size: $\varnothing \sim 10$ mm) operating in reflectance mode. The instrument has a spectral resolution of 3 nm at 700 nm and 10 nm at 1400/2100 and measurements were calibrated with a white Spectralon (PTFE) standard.

Dynamic Mechanical Analysis (DMA) is a technique used to measure the viscoelastic properties of materials, in particular polymers. An RSA III Rheometrics Analyzer was used to take all measurements with the standard TA Orchestrator Software. Samples were prepared for DMA by cutting and sanding small pieces of the desired formulations to approximately 1 - 1.5mm in thickness, with widths ranging from 7 to 14mm (Fig. 16). This step proved somewhat difficult, as some of the samples originally selected were brittle and prone to snapping with even gentle applied force.

Width and thickness measurements were taken in three different locations, the mean average calculated, then entered into the software to account for differences in dimensions. Samples were placed on a 10mm three-point bending tool for analysis. The temperature was held between 25 and 26° C, and the strain at approximately .005% for single-point tests and frequency sweeps. Dynamic single-point measurements were taken with frequency held at 1 Hz, while logarithmic frequency sweep data was defined by a range between 1 and 50 Hz.

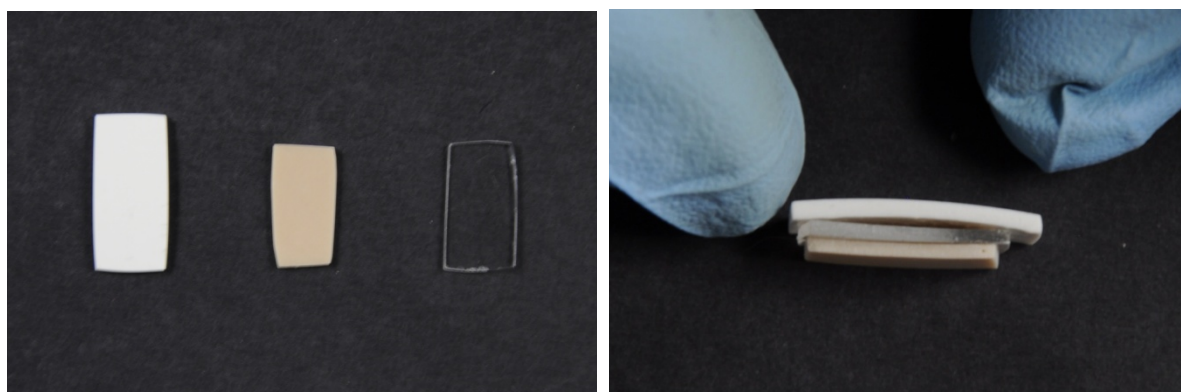


Fig. 16: Samples for DMA following cutting and sanding. The brittle nature of the gels caused some difficulty, hence the variation in size, though this was accounted for with instrumental software.

Scanning Electron Microscopy (SEM) was used to analyze the bulk microstructure of the final materials. Samples were cut (~ 1 x 0.5 cm), sanded on one side and attached to the aluminum stub with double-sided carbon tape. Cross-sections (break) of the samples were examined with a NOVA NanoSEM 230 (FEI) instrument equipped with an EDS detector (UltraDry, Thermo Scientific). Each sample was imaged at different magnifications in variable pressure mode and with a 10 kV acceleration voltage.

5. Experimental Results and Discussion

5.1. Qualitative Tests

5.1.1. TEOS and TEOS/PDMS Mixtures

The composition and properties of TEOS and TEOS/PDMS mixtures are given in Table 2. DA ethyl silicate showed more cracking in comparison to D40, which can be attributed to the higher percentage of monomers in DA. At 75% RH, ethyl silicate monomers react too fast and form a highly cross-linked network with larger gel particles. Rapid cross-linking explains the opaque white color of the samples with DA, as opposed to the transparency of the gel obtained with the D40 ethyl silicate (Fig. 17).

Table 2: Composition (weight %) and properties of TEOS and TEOS-PDMS mixtures							
Trial #	Composition			Properties			
	TEOS		PDMS	Shrinkage	Cracking	Strength	Flexibility
	DA	D40					
1-1	100.0			-	-	+	+
1-2		100.0		-	-	-	-
1-3		95.0	5.0	-	+	+	+
LR-2		80.0	20.0	+	+	++	+
LR-3		60.0	40.0	++	+++	++	+++

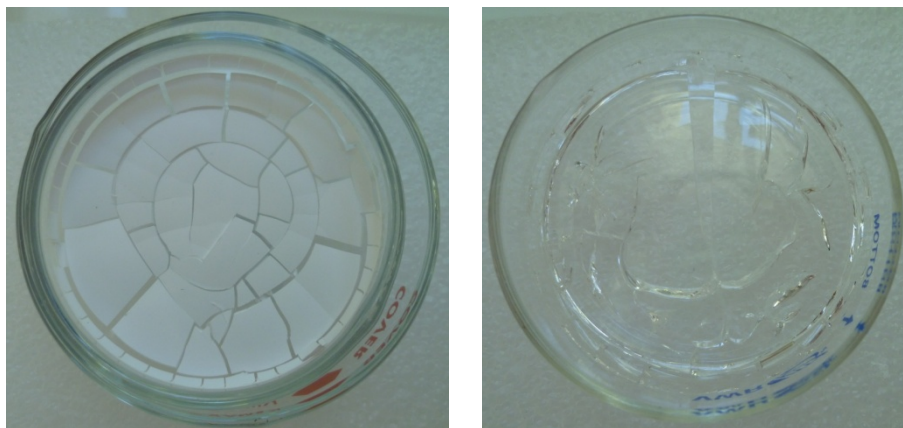


Fig. 17: Morphology and color of the gels obtained with DA (left) and D40 (right) ethyl silicates after reaction at 75% RH

The addition of a small amount of PDMS to D40 showed only mildly less cracking, but with slightly better strength and flexibility. However, as the concentration of PDMS was increased (LR-2 and LR-3), results improved across the board, with much less shrinkage and cracking, and higher strength and flexibility. This is likely because the PDMS chains impart elasticity to the silica-PDMS hybrid network.

5.1.2. TEOS and TEOS-PDMS formulations with various fillers

Quartz particles were added to the TEOS and TEOS/PDMS mixtures to provide the necessary consistency and bulk properties required for a grout formulation (Table 3). Both 3:2 and 1:1 solid to liquid ratios were evaluated, but the 1:1 ratio was finally selected for later trials. A 3:2 ratio seemed to overload the formulation with solid particles, often showing significant separation, though this was not observed systematically. Early trials with DA yielded poor results, often with pronounced cracking and poor strength and flexibility. It was therefore decided to use only D40 as a base for the formulations.

In general, the formulations with smaller particles (M5) showed less shrinkage and cracking as well as better strength than those containing larger particles (M15 and M40). The use of smaller particles (M5) resulted also in less separation compared to M15 and M40. This could be explained by a better dispersion of the small quartz particles and the development of stabilization interactions that positively counteract gravity effects.

Furthermore, the addition of quartz particles to TEOS/PDMS mixtures generally produced final gels with improved properties in terms of cracking and strength, particularly for the formulations containing the fine grade quartz particles (M5). The presence of PDMS tended also to increase the flexibility, though the effect is not as pronounced within the concentration range (2 to 10%) used for these trials.

Table 3: Composition and properties of TEOS- and TEOS/PDMS-based formulations with the addition of various solid fillers

TRIAL #	S:L	Composition							Properties					
		SOLID				LIQUID			Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		M5	M15	M40	HGS	TEOS		PDMS						
DA	D40													
1-4	3:2	60.0				40.0			+	++	+	-	+	+
1-5	3:2			60.0		40.0			+	-	++	+	-	-
1-6	3:2	60.0					40.0		+	++	+	++	+	+
2-1	3:2		60.0				40.0		+	-	+	+	++	-
1-7	3:2			60.0			40.0		+	-	+	+	++	+
1-8	1:1	50.0				50.0			+	++	++	-	-	-
1-9	1:1			50.0		50.0			+	++	+	-	-	-
1-10	1:1	50.0					50.0		+	++	-	++	++	+
2-2	1:1		50.0				50.0		+	-	-	+	++	+
1-11	1:1			50.0			50.0		+	-	+	-	+	+
1-12	3:2	60.0					38.0	2.0	+	++	-	+	++	++
1-13	3:2			60.0			38.0	2.0	+	++	-	-	+	+
1-14	1:1	50.0					47.5	2.5	+	++	+	++	++	+
2-11	1:1	50.0					47.5	2.5	+	++	-	+	++	+
2-4	1:1		50.0				47.5	2.5	+	-	-	+	+++	+
1-15	1:1			50.0			47.5	2.5	+	-	+	-	+	+
2-5	1:1	50.0					45.0	5.0	+	++	-	+	+++	+
2-6	1:1			50.0			45.0	5.0	+	-	-	-	+	+
2-7	1:1	50.0					40.0	10.0	+	++	-	+	+++	+
2-8	1:1			50.0			40.0	10.0	+	-	-	-	+	+
6-13	1:1				50.0*		40.0	10.0	+	-	-	+	+++	++
* % in volume														

* % in volume

Hollow glass spheres (HGS) were added to some trials to lower the density of the solid material and to minimize separation. When HGS were the only solids in the formulation (6-13), there was a marked inverse phase separation due to their lower density, but surprisingly, strength and flexibility were relatively good.

For trials 1-14 and 2-11, which had the same formulation, the mixing order of the components did not seem to affect much the final properties, whether liquids were added to solids (1-14), or vice versa (2-11). The influence of this parameter, however, would require more systematic and comparative trials to be fully explored. In general, trials were prepared by adding liquids to solids when not stated otherwise.

5.1.3. Formulations with sepiolite B5 and B10

Sepiolite was tested as an additive both for its form factor that could potentially impart flexibility and strength, as well as its thickening properties to control viscosity and reduce flow. The composition and properties of selected trials with sepiolite are given in Table 4. When sepiolite was added to TEOS (R-75-4), the mixture showed reduced separation, slightly less cracking, and higher strength and flexibility in comparison to pure TEOS. For more complex formulations, early trials were formulated with both B5 and B10 grades; however, no significant differences in properties were discerned. As a result, B10 was selected for most trials to simplify comparisons.

Several trials, such as those with a 3:2 solid:liquid ratio with M5 and as little as 1% sepiolite, or others with a high percentage of sepiolite (4 to 5%) resulted in very viscous, nearly unworkable, mixtures and are not reported here. The lack of workability can be attributed to the thickening effect of the sepiolite, which effectively surpassed the particle loading capacity of these formulations. When M5 was replaced with M15 or M40 in formulations with a 3:2 solid:liquid ratio, workability was better, but final properties remained only satisfactory. However, for 1:1 solid:liquid ratio trials with M5, overall properties were improved by the addition 1% sepiolite, though increasing it to 3%, seems to negatively affect the strength and flexibility. The best results, especially regarding cracking and strength, were actually obtained for 1:1 formulations containing M5, 1 to 3% of sepiolite and increasing amounts of PDMS.

Table 4: Composition and properties of formulations with sepiolite B5 and B10.														
TRIAL #	S:L	Composition							Properties					
		Quartz			Sepiolite		TEOS	PDMS	Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		M5	M15	M40	B5	B10								
R-75-4	1:9					10.0	90.0		+	++	-	++	++	+
4-1	1:1	49.0				1.0	50.0		+	++	+	++	++	+
4-9	1:1	47.0				3.0	50.0		+	++	-	+	+	+
3-5	1:1			49.0		1.0	50.0		+	-	+	+	+	-
3-2	1:1			49.0	1.0		50.0		+	-	-	+	+	-
3-4	3:2			59.0		1.0	40.0		+	+	+	+	+	-
3-1	3:2			59.0	1.0		40.0		+	+	++	++	+	-
3-6	3:2		59.0			1.0	40.0		+	+	-	+	++	+
3-3	3:2		59.0		1.0		40.0		+	+	+	+	++	+
3-7	3:2			59.0	1.0		38.0	2.0	+	-	+	+	+	-
3-11	3:2			59.0		1.0	38.0	2.0	+	-	+	+	+	-
3-9	3:2		59.0		1.0		38.0	2.0	+	+	+	++	++	+
4-2	1:1	49.0				1.0	45.0	5.0	+	++	+	++	++	+
4-3	1:1	49.0				1.0	40.0	10.0	+	++	-	++	+++	+
4-10	1:1	47.0				3.0	45.0	5.0	+	++	-	+	++	+
4-11	1:1	47.0				3.0	40.0	10.0	+	++	+	+++	++	+
4-12	1:1	47.0				3.0	30.0	20.0	+	++	++	+++	++	+++

With regards to the combined effect of the sepiolite and the PDMS, the latter decreases the modulus by lending elasticity to the otherwise rigid silicate structure, reducing capillary pressures and cracking (Mackenzie and Bescher 1998; Salazar-Hernández et al. 2010; Shirosaki et al. 2012). The sepiolite, on the other hand, apparently enhances this effect by providing structural reinforcement and helping to reduce the shrinkage, and thus the cracking. It should be mentioned, however, that the potential of the sepiolite is probably not fully exploited by manually mixing the components, which is not ideal and in some cases might not provide enough shear to achieve an adequate dispersion of this additive.

5.1.4. TEOS/PDMS with various types of fillers and additives

Based on the results discussed prior, additional trials were prepared in an attempt to optimize the contribution of the various components used in the formulations. Most of the trials were based on the use of a M5/M40 mixture together with sepiolite, TEOS and PDMS in various proportions (Table 5). In general, the results showed an improvement in the final properties, particularly in that there was no separation despite the use of M40, as well as less shrinkage, much less cracking, and higher strength. Flexibility was also increased in direct correlation with the amount of PDMS, though high levels (30%) might have also imparted too much hydrophobicity to the material, thus negatively affecting adhesion properties.

Table 5: Composition and properties of TEOS/PDMS mixtures with various types of solid fillers and additives													
TRIAL #	S:L	Composition						Properties					
		Quartz/Glass			Sepiolite	TEOS	PDMS	Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		M5	M40	Others	B10								
4-6	1:1	23.5	23.5		3	50		+	++	-	+	++	+
4-7	1:1	23.5	23.5		3	45	5	+	++	-	+	++	+
4-8	1:1	23.5	23.5		3	40	10	+	++	+	+++	++	+
5-1	1:1	24.0	24.0		2	40	10	+	++	+	+++	+++	++
5-2	1:1	24.0	24.0		2	30	20	+	++	+	+++	++	++
5-3	1:1	24.0	24.0		2	20	30	+	++	++	+++	++	+++
5-4	1:1	23.0	23.0		4	40	10	-	++	-	++	+++	++
5-5	1:1	23.0	23.0		4	30	20	+	++	++	+++	++	++
5-6	1:1	23.0	23.0		4	20	30	+	++	++	+++	++	+++
5-7	1:1	9.6	38.4		2	40	10	+	+	+	++	++	++
5-8	1:1	9.6	38.4		2	30	20	+	++	++	+++	+++	++
5-9	1:1	9.4	37.6		3	40	10	+	++	+	++	+++	++
5-10	1:1	9.4	37.6		3	30	20	+	++	++	+++	+++	++
5-11	1:1	9.0	36.0		5	40	10	-	++	+	+++	++	++
5-12	1:1	9.0	36.0		5	30	20	-	++	+	+++	++	++
6-75-6	1:1	12.0		36.0 (Sil75)	2	40	10	+	+	+	++	-	-
6-75-7	1:1	12.0		36.0(GS40)	2	40	10	+	-	-	-	-	+
6-75-12	1:1	12.0		36.0* (HGS)	2	40	10	+	++	-	+	+	++
* % in volume													

Replacement of M40 in the solid phase by coarser grades of ground quartz (Sil-75), sand (GS40) or HGS had poor results compared to the trials formulated with a mixture of M5 and M40 ground quartz.

5.1.5. Silanes

The composition and properties of formulations containing AMEO and GLYMO silanes are given in Table 6. For trials containing AMEO at various concentrations, the final product was almost always characterized by an extreme amount of shrinkage and cracking, as well as very low strength and flexibility (4-4, 5-13, 5-15). In fact, only one trial (6-75-9) with M5 as a filler showed high strength and flexibility, a result which necessitates confirmation before making any interpretation. On the other hand, the presence of GLYMO could be associated with minimal shrinkage and cracking as well as good strength and flexibility (4-5, 5-14, 5-16).

Table 6: Composition and properties of formulations with AMEO and GLYMO														
TRIAL #	S:L	Composition							Properties					
		Solid			Liquid				Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		M5	M40	B10	TEOS	PDMS	Silanes							
							AMEO	GLYMO						
6-75-11					88.0	10.0	2.0		+	++	-	-	+	+
6-75-9	1:1	50.0			38.0	10.0	2.0		+	+	-	-	+++	++
6-75-10	1:1	50.0			38.0	10.0		2.0	+	++	+	++	-	-
4-4	1:1	49.0		1.0	44.0	5.0	1.0		+	++	-	-	-	-
4-5	1:1	49.0		1.0	44.0	5.0		1.0	+	++	+	++	+++	+
5-13	1:1	9.6	38.4	2.0	36.0	10.0	4.0		+	++	-	-	-	-
5-14	1:1	9.6	38.4	2.0	36.0	10.0		4.0	+	++	+	+++	++	++
5-15	1:1	9.6	38.4	2.0	32.0	10.0	8.0		+	++	-	-	-	-
5-16	1:1	9.6	38.4	2.0	32.0	10.0		8.0	+	++	+	++	++	++

5.1.6. Influence of RH

There were significant differences in strength between trials in different humidity conditions, as well as a few moderate discrepancies. A comparison of the properties for selected formulations placed at 75 and 25% RH are given in Table 7. The most pronounced differences were observed for the trials with the silanes AMEO and GLYMO, suggesting that RH levels have a strong effect on the resulting gel. For the trial containing AMEO and M5 (6-75-9) at 75% RH, the strength and flexibility were higher, compared to the same formulation placed in drier conditions. On the other hand, for the trials with GLYMO (6-10), better results were obtained at 25% RH. For the trials without silanes, differences were more subtle and difficult to assess visually.

Table 7: Comparison of selected formulations at 75 and 25% RH														
TRIAL #	S:L	Composition							Properties					
		Solid			Liquid				Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		M5	M40	B10	TEOS	PDMS	Silanes							
							AMEO	GLYMO						
6-75-1	1:1	24.0	24.0	2.0	40.0	10.0			+	+	-	++	++	++
6-25-1	1:1	24.0	24.0	2.0	40.0	10.0			+	-	+	++	++	++
6-75-3	1:1	12.0	36.0	2.0	40.0	10.0			+	+	+	++	++	++
6-25-3	1:1	12.0	36.0	2.0	40.0	10.0			+	+	+	++	+	+
6-75-9	1:1	50.0			38.0	10.0	2.0		+	+	-	-	+++	++
6-25-9	1:1	50.0			38.0	10.0	2.0		+	-	+	+	+	+
6-75-10	1:1	50.0			38.0	10.0		2.0	+	++	+	++	-	-
6-25-10	1:1	50.0			38.0	10.0		2.0	+	++	+	++	+++	++

5.2. Quantitative Tests

5.2.1. Sol reactivity and gel formation

Weight loss was measured as a function of time for a set of reference trials and a set of more complex formulations. The measurements were taken in order to estimate the overall kinetics of the process leading to the formation of a solid material (gel) from the initially liquid mixture (sol), the phase in which the hydrolysis and condensation of the TEOS occurs. For the more complex formulas, selected trials were also concomitantly analyzed with UV-Vis-NIR spectroscopy in an attempt to identify and follow the evolution of reactive functional groups and other reaction products. For both sets, weight loss experiments were conducted in two different relative humidity conditions (~25 and ~75%).

5.2.1.1. Weight loss experiments

5.2.1.1.1. Reference set

The different reference trials consisted of relatively simple formulations including pure TEOS (DBTL-catalyzed), TEOS and PDMS, and liquid-solid mixtures with ground quartz (M5) and sepiolite (B10); some of them were also duplicated in larger glass dishes (LR) to assess potential surface effects on reaction rates (Table 8).

Table 8: Composition of reference set trials					
TRIAL #	S:L	Solid		Liquid	
		M5	B10	TEOS	PDMS
R-75-1				100	
R-75-2				80	20
R-75-3	1:1	50		50	
R-75-4	1:9		10	90	
R-75-5*	1:9		10	90	
R-25-1				100	
R-25-2				80	20
R-25-3	1:1	50		50	
LR-75-1				100	
LR-75-2				80	20
LR-75-3				60	40
LR-75-4	1:9		10	80	10
* B10 dried at 110°C for 6 hours					

For all trials, the weight loss (W_x), normalized to the initial weight (W_0) and expressed as a percentage, was monitored over 300 hours and predictably increased as a function of time with a progressive rate decrease (Fig. 18, 19, 20 and 21). In comparison to the weight loss achieved after 300 hours, most loss occurred within the first 50 hours, indicating that the hydrolysis of the

ethoxy groups leading to the formation and release of ethanol was relatively fast. In addition, most formulations appeared to be ‘solid’ after 12 hours; in some cases, this occurred in association with crack formation, showing that condensation reactions responsible for the gelation had started as well. A closer look at the kinetics of the process in the first 50 hours indicates that, after a short induction period (~ one to two hours) and until a reaction time of about 36 hours, the weight loss is highly correlated to the square root of time with coefficient of determination (R^2) values close to one. Such a linear trend points towards a diffusion controlled process involving the transfer of water molecules from the ambient atmosphere (75 and 25% RH.) and the hydrolysis/condensation of the TEOS.

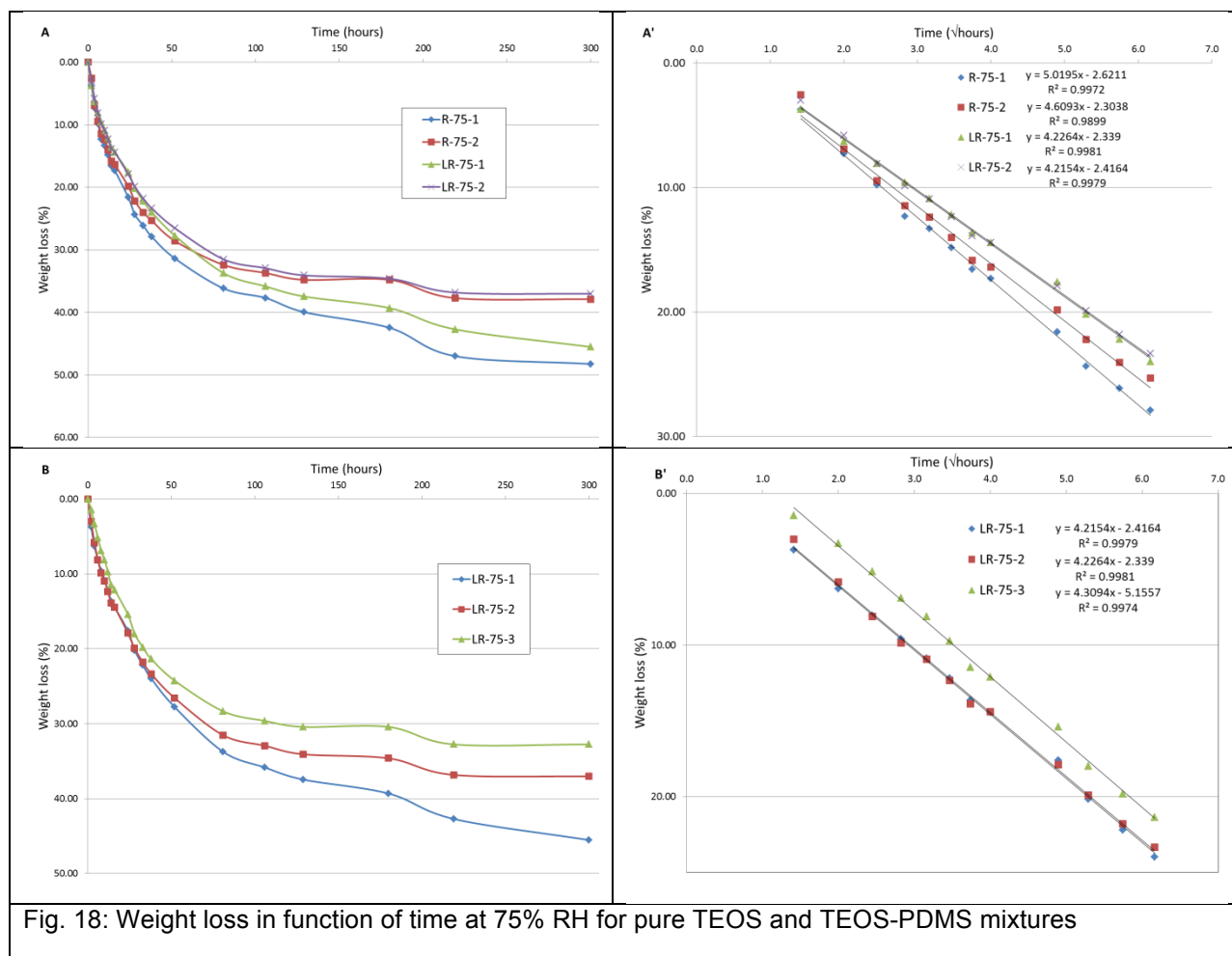


Fig. 18: Weight loss in function of time at 75% RH for pure TEOS and TEOS-PDMS mixtures

In comparison to pure TEOS, the addition of 20% of PDMS seems to increase the weight loss rate in the first 36 hours independently of the glass dish size as the slope values are very close or slightly lower (Fig. 18, A') for the TEOS-PDMS mixture when these values, based on the amount of TEOS, should be lower by a factor of 0.8 if the PDMS would not affect the process. This effect is even more pronounced for the trial containing 40% PDMS (Fig. 18, B') and could be explained by a higher diffusion coefficient of water in the TEOS-PDMS mixtures and/or an increase in the TEOS hydrolysis reaction rate.

For the TEOS and TEOS-PDMS trials placed at a relative humidity of 25%, weight loss rates in the first 36 hours are significantly lower than at 75% RH (Fig. 19). This difference occurs also for all the other trials and can be attributed to fewer water molecules available for the hydrolysis reactions at low relative humidity.

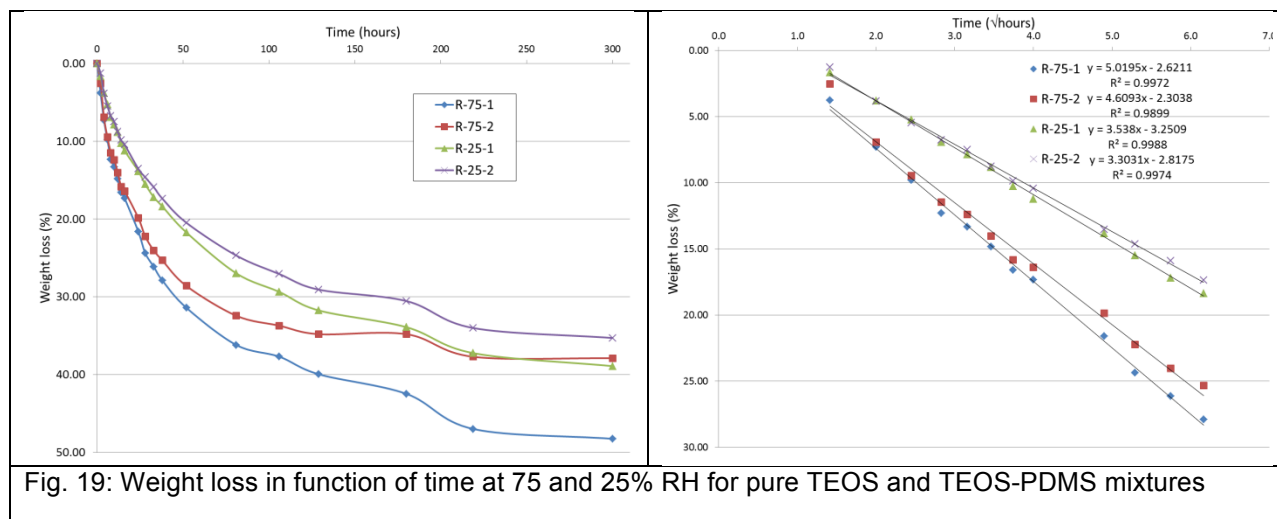


Fig. 19: Weight loss in function of time at 75 and 25% RH for pure TEOS and TEOS-PDMS mixtures

The addition of finely ground quartz (M5) to TEOS (1:1 in weight) results in a slower weight loss rate compared to pure TEOS at both 25 and 75% RH. (Fig. 20, A). This apparent decrease is directly related to the lesser amount of TEOS in the mixture and is reflected in the slope values obtained when the weight loss is plotted as a function of the square root of time (Fig. 20, A'). However, with half the amount of TEOS, the slope ratio should be close to two while it is about 1.75 at both 75 and 25% RH. This indicates a slightly higher weight loss rate than predicted, which could be due to the presence of water adsorbed on the ground quartz.

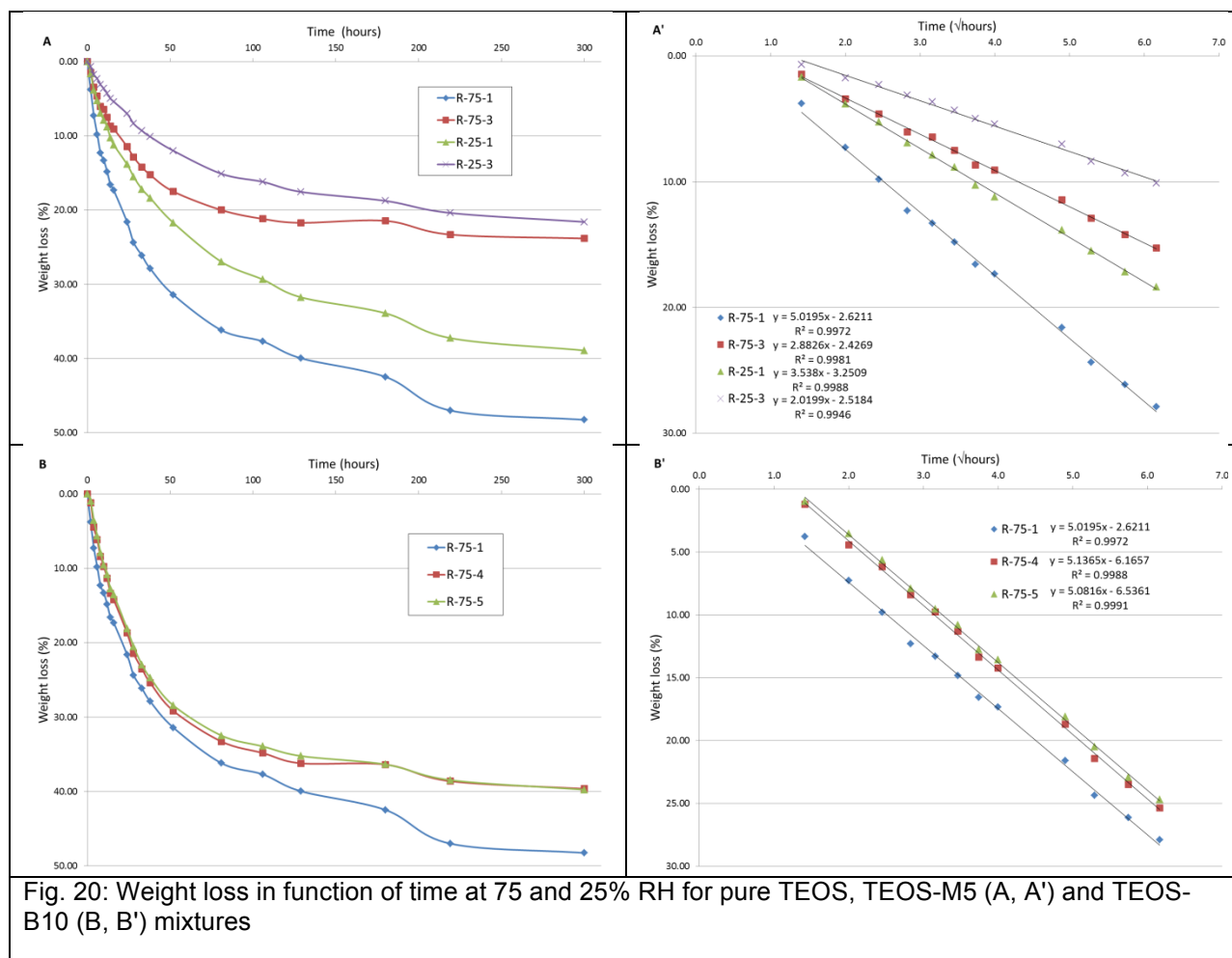


Fig. 20: Weight loss in function of time at 75 and 25% RH for pure TEOS, TEOS-M5 (A, A') and TEOS-B10 (B, B') mixtures

For the TEOS-B10 mixtures, the addition of sepiolite does not significantly modify the weight loss rates as they are very close to the one of pure TEOS though with slightly higher slopes than predicted (Fig. 20, B and B'). Interestingly, the weight loss curves and slope values are similar for the mixtures prepared with non- and pre-dried² sepiolite suggesting that the water molecules filling the structural channels of the clay do not contribute to the hydrolysis reaction of the TEOS. For the trial containing 10% PDMS in addition to the sepiolite, the weight loss rate is slower with nevertheless a slope value still above the one predicted by the amount of TEOS (Fig. 21).

² Drying resulted in a weight loss of about 5% due primarily to the removal of zeolitic water.

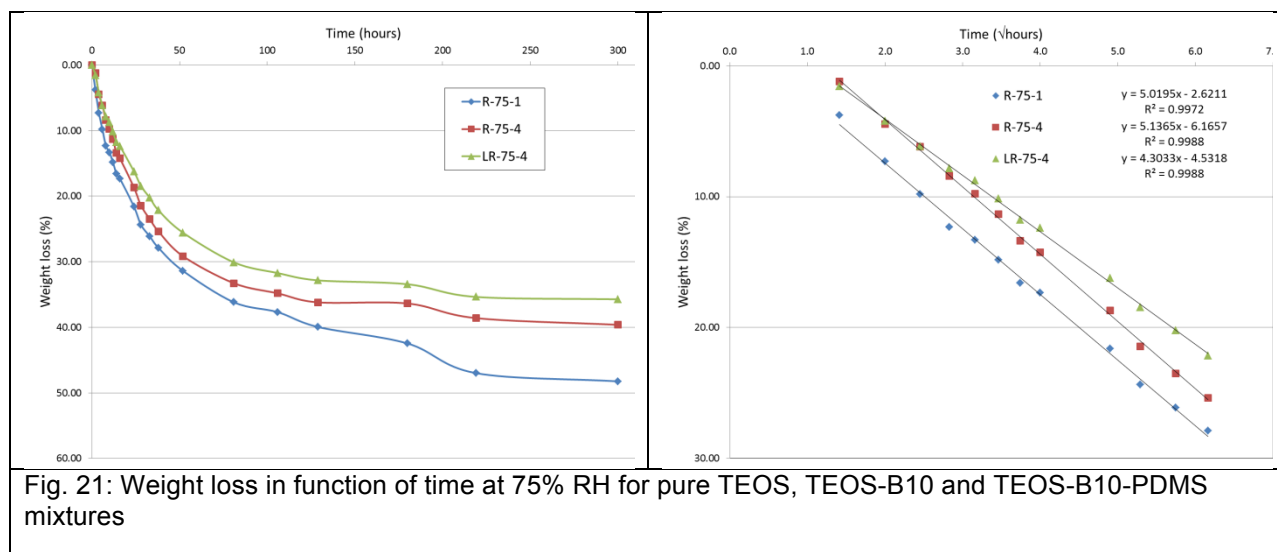


Fig. 21: Weight loss in function of time at 75% RH for pure TEOS, TEOS-B10 and TEOS-B10-PDMS mixtures

In addition to the analysis of the kinetics of the sol-gel process, the extent of the TEOS transformation was evaluated based on the total weight loss at the end of the experiments. For pure TEOS (D40), when the hydrolysis and condensation reactions are complete, the amount of silica gel formed represents about 41% of the initial weight of TEOS. Furthermore, since the weight loss achieved after 300 hours is mainly correlated to the percentage of TEOS in the formulations (Fig. 18, 19, 20 and 21), the degree of transformation was estimated by the ratio (expressed in %) of the weight loss after 300 hours (W_{300h}) to the maximum weight loss (W_{max}) corrected by the amount of TEOS in order to allow a direct comparison between the trials (Table 9). It can be observed that after 300 hours none of the formulations have completely reacted as the ratios span from 65.9 to 89.5%. When comparing the trials at 25 and 75% RH, the ratios are always higher for the latter in accordance with the faster kinetics discussed previously. Following the same trend, the trial with 40% of PDMS presents the highest degree of transformation (89.5%) confirming the effect of the PDMS. More generally, it seems that there is a relative consistency between the degree of transformation after

300 hours and the weight loss rate in the first 50 hours. However, it should also be noticed that for all the trials containing sepiolite and despite relatively high weight loss rates, the ratios are rather low, around 75%, a result that would need to be studied further for a proper explanation.

Table 9: Comparison between the weight loss after 300 hours (W_{300h} in %) and the maximum weight loss (W_{max} in %) normalized to the amount of TEOS in the formulation

	R-75-1	R-75-2	R-75-3	R-75-4	R-75-5	R-25-1	R-25-2	R-25-3	LR-75-1	LR-75-2	LR-75-3	LR-75-4
W_{300h}	48.2	37.9	23.8	39.6	39.7	38.9	35.3	21.6	45.5	37.0	32.7	35.7
W_{max}	59.0	47.2	29.5	53.1	53.1	59.0	47.2	29.5	59.0	47.2	36.6	47.2
$(W_{300h}/W_{max})*100$	81.8	80.3	80.7	74.6	74.8	65.9	74.8	73.2	77.2	78.4	89.5	75.7

5.2.1.1.2. Complex Formulations

The behavior of more complex formulations does not differ much from the reference trials in that it is primarily the transformation of the TEOS, which contributes to the overall weight loss. There are, however a few interesting results which will be discussed below in more detail. Weight loss was measured over a period of about 24 days for a series of fourteen trials (Table 10)³ at both 75 and 25% RH. As the first weight measurements could be done only after 12 hours, kinetics of the reactions will be discussed qualitatively. It should be also mentioned that for all trials, an unexpected weight increase was recorded for the measurements at 466 hours, which could be due to an uncontrolled temperature drop in the room where the experiments were carried out, though an experimental error cannot be ruled out.

³ Trials also analyzed with UV-Vis-NIR spectroscopy are shaded in grey.

Table 10: Composition of the complex formulations

TRIAL #	S:L	SOLID				LIQUID				Mixing order
		M5	M40	Others	B10	TEOS	PDMS	AMEO	GLYMO	
1	1:1	24	24		2	40	10			M5 + D40 + B10 + M40 + PDMS
2	1:1	24	24		2	30	20			M5 + D40 + B10 + M40 + PDMS
3	1:1	12	36		2	40	10			M5 + D40 + B10 + M40 + PDMS
4	1:1	12	36		2	30	20			M5 + D40 + B10 + M40 + PDMS
5	1:1		48		2	40	10			M40 + D40 + B10 + PDMS
6	1:1	12		36 (Sil-75)	2	40	10			M5 + D40 + B10 + Sil 75 + PDMS
7	1:1	12		36 (GS-40)	2	40	10			M5 + D40 + B10 + GS-40 + PDMS
8	1:1	12		34 (GS-40)	4	40	10			M5 + D40 + B10 + GS-40 + PDMS
9	1:1	50				38	10	2		M5 + D40 + PDMS-OH + silane
10	1:1	50				38	10		2	M5 + D40 + PDMS-OH + silane
11						88	10	2		D40 + PDMS-OH + silane
12	1:1	12		36 (HSP)*	2	40	10			M5 + D40 + B10 + HSP + PDMS
13	1:1			50 (HSP)*		40	10			D40 + HSP + PDMS
14					5	85	10			B10 + D40 + PDMS

* % in Volume

The morphologies of the gels obtained for each of the fourteen trials after the reaction at 75% RH and in drier conditions are relatively similar (Fig. 22), and are consistent with the qualitative assessments given previously for some of them.

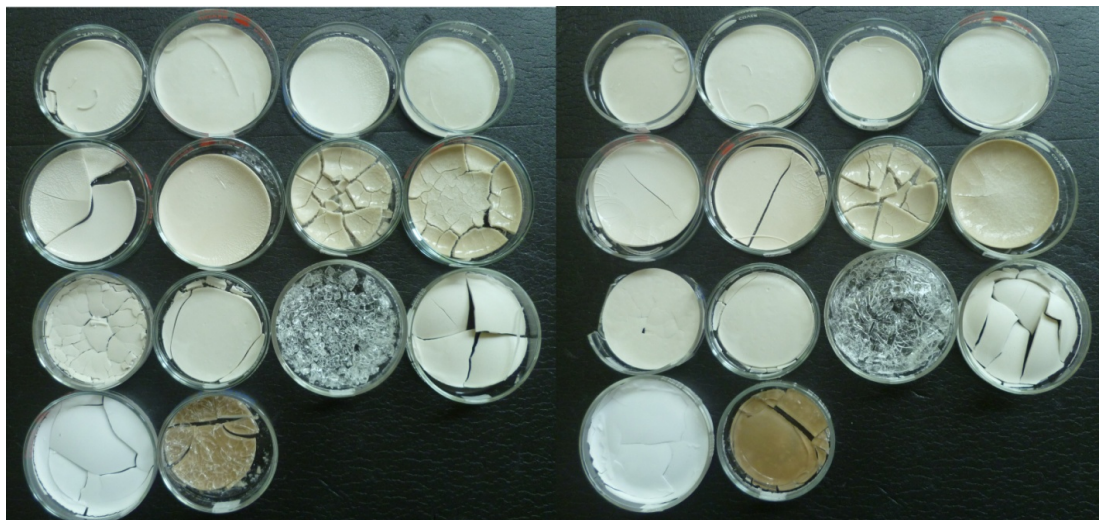


Fig. 22: Morphology of the gels after 26 days at 75 (left) and 25% RH (right). Trials 1 to 14 from top left to right and down

For the trials 1, 2, 3 and 4, weight losses are almost identical during the first forty hours and apparently independent of the type of quartz filler or relative proportions of M5 and M40 (Fig. 23, A). However, as trials 2 and 4 contain twice as much PDMS, the kinetics of hydrolysis are actually faster for those, a tendency already noticed for the reference trials containing higher amounts of PDMS. At 25% RH, weight losses follow the same trend, though at a slower rate, and the effect of the PDMS is even more visible in the first two days despite some experimental variability in the measurements (Fig. 23, A').

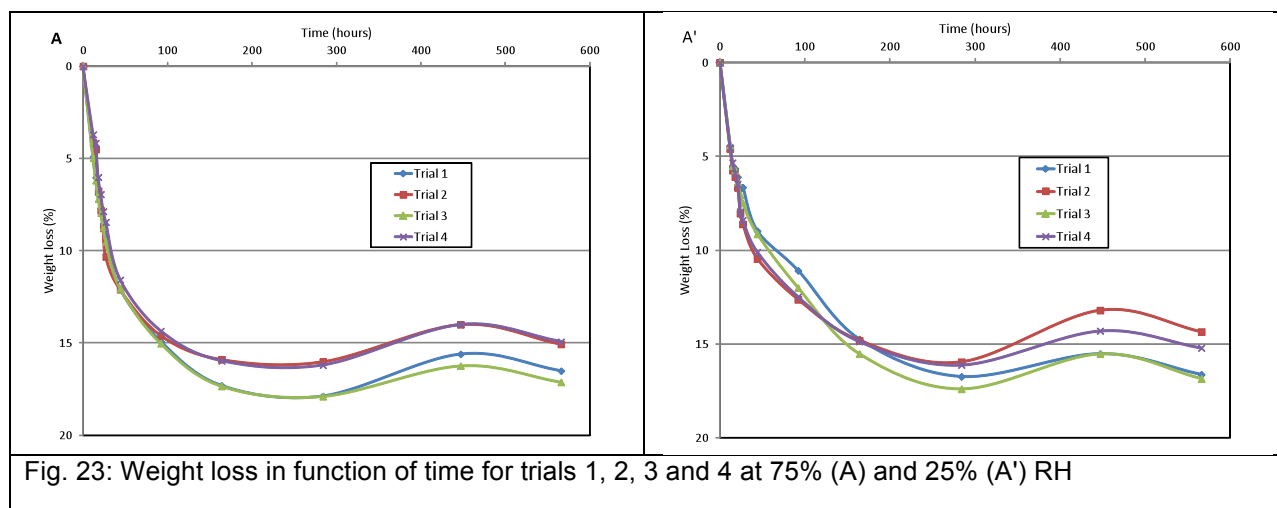
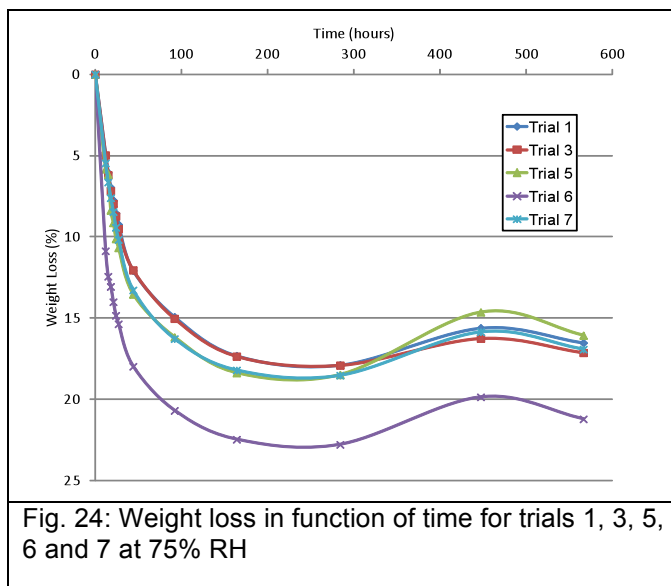


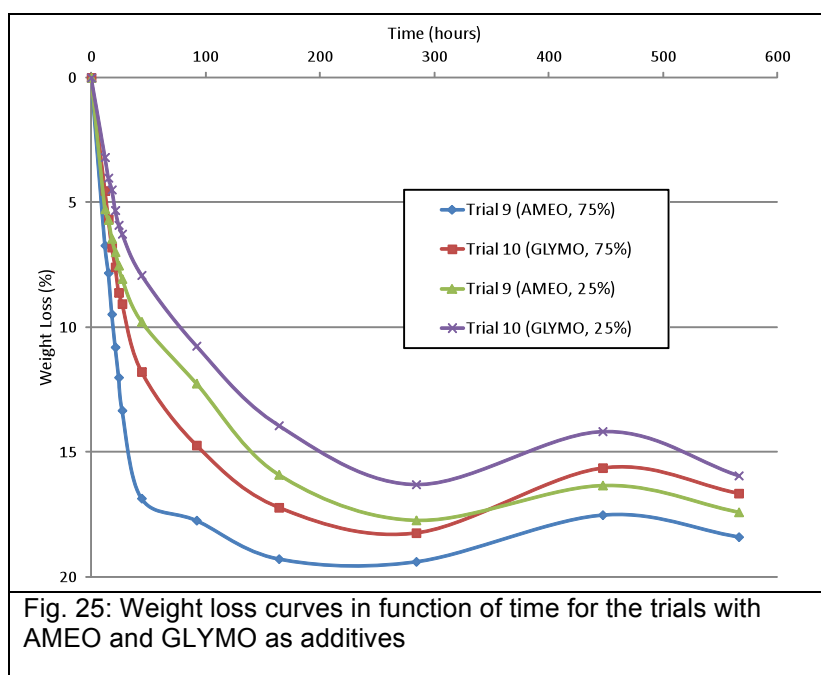
Fig. 23: Weight loss in function of time for trials 1, 2, 3 and 4 at 75% (A) and 25% (A') RH

The weight loss curve for trial 6 shows a peculiar pattern in comparison to others that contain the same amount of TEOS and PDMS (Fig. 24). The weight loss rate is much faster and the degree of transformation of the ethyl silicate after 24 days is also higher. This behavior seems to be related to the quartz filler (Sil-75) as it is the only parameter that differs in the formulation.

Although this remains difficult to explain without additional data, it could be possible that besides quartz, the presence in this filler grade of other elements such as aluminum in the form of oxides or alumino-silicates could contribute to an acceleration of the hydrolysis reaction rate.



The weight loss curves for the trials with the silanes AMEO and GLYMO (trials 9 and 10) are consistent with the visual observations and qualitative evaluations. Both silanes show a tendency for accelerated weight loss, but the effect is much more pronounced with AMEO (Fig. 25) which at 75% RH, because of its high reactivity towards water and the probable catalyst effect of the amine group, results in a weight loss within the first two days close to the one obtained after 24 days.



The importance of the role of water in the presence of this silane is confirmed by the experiment at 25% RH, for which the effect is less apparent with a profile of the weight loss curve becoming closer to the one with GLYMO (trial 10) though the faster rate during the first day is still clearly visible.

Finally, as for the reference trials, it is interesting to look at the degree of transformation achieved after 24 days by comparing the corresponding weight loss to the maximum weight loss approximately defined by the amount of TEOS in the formulation (Table 11). The values of the ratios for the experiments at 75 and 25% RH vary from 68.2 to 89.8% and 67.8 to 85.9% respectively, and indicate that the hydrolysis and condensation reactions are not complete after 24 days.

Table 11: Comparison between the weight loss after 566 hours at 75 and 25% RH (W_{566h} in %) and the maximum weight loss (W_{max} in %) based on the amount of TEOS in the formulation

	Trials													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$W_{75_{566h}}$	16.5	15.1	17.1	14.9	16.1	21.2	16.9	16.3	18.4	16.6	41.9	25.6	32.3	38.1
$W_{25_{566h}}$	16.6	14.4	16.9	15.2	17.2	16.0	16.4	16.9	17.4	15.9	36.4	24.5	30.4	34.9
W_{max}	23.6	17.7	23.6	17.7	23.6	23.6	23.6	23.6	23.2	23.2	52.8	34.9	42.9	50.1
$(W_{75_{566h}}/W_{max})*100$	69.9	85.3	72.5	84.2	68.2	89.8	71.6	69.1	79.3	71.6	79.4	73.4	75.3	76.0
$(W_{25_{566h}}/W_{max})*100$	70.3	81.3	71.6	85.9	72.9	67.8	69.5	71.6	75.0	68.5	68.9	70.2	70.9	69.7

Despite the higher weight loss rates in the first two days mentioned earlier for the experiments carried out at 75% RH, it appears that after 24 days, the degree of transformation is often very close to the one achieved in drier conditions, in particular for trials 1, 2, 3 and 4. For these trials, the ratio values also clearly show that higher PDMS concentrations increase both the hydrolysis reaction rate and the degree of transformation after 24 days. Conversely, for the trial containing AMEO, and to a lesser

extent for the one with GLYMO, despite high reaction rates during the first days, the degree of transformation after 24 days remains at an intermediate level.

5.2.1.2. Monitoring of TEOS reactivity with UV-Vis-NIR spectroscopy

Reflectance measurements in the UV-Vis-NIR spectral range were carried out during the weight loss experiments for selected trials (Table 10) Due to a technical problem, the first measurement was taken after 12 hours and thereafter every time when weight was measured. The correspondence between spectra references and time is given in Table 12. For all the trials, it is expected that the main changes in the spectral signature will correspond to

Table 12: Link between spectral references and time	
Spectra Ref.	Time (hours)
Ref_00000	12
Ref_00001	15
Ref_00002	18
Ref_00003	21
Ref_00004	24
Ref_00005	27
Ref_00006	44
Ref_00007	92
Ref_00008	164
Ref_00009	284
Ref_00010	447
Ref_00011	566

overtones and combination vibrations in the near-infrared (NIR) related to TEOS and PDMS as well as to the silanes (trials 9 and 10) though the latter were added in much lower concentration (2%). A brief screening of the spectra collected for trials 1, 3 and 7 at 75% RH has shown that they are very similar, which is consistent with their composition as they only differ by the type of quartz filler added to the formulation. Therefore, trial 1 was used to

study spectral bands identification and evolution in relation to the transformation of TEOS during the sol-gel process.

The reflectance spectra collected over time (Fig. 26) indicate that there are several regions of interest in the NIR spectral domain where the main absorptions occur:

- from ~2200 to ~2450 nm with primarily the C-H stretching (ν) and bending (δ) combination modes ($\nu + \delta$) related to the presence of ($-\text{CH}_3$) and ($-\text{CH}_2-$) groups;
- around 1900 nm for combination modes involving water molecules
- from ~1650 to ~1780 nm for the first overtone of the C-H stretching:
 $2\nu(\text{C-H})$
- from 1350 to 1480 nm for the first overtone of the O-H stretching:
 $2\nu(\text{O-H})$
- around 1200 and 900 nm for the second and third overtones of the C-H stretching: 3ν and $4\nu(\text{C-H})$



Fig. 26: Reflectance spectra for Trial 1 with main absorption features in the NIR

In order to help in the identification of specific groups, relevant absorption features in the near-infrared were compiled from literature data (Table 13).

Table 13: Main vibrational absorption bands in the NIR relevant to the compounds in the formulations and their reaction products			
PDMS		TEOS / Silica gel / H ₂ O / Ethanol	
Wavelength (nm)	Vibrational modes	Wavelength (nm)	Vibrational modes
2401	$\nu_s(\text{CH}_3) + \delta_s(\text{CH}_3)$	2295	$\nu_a(\text{CH}_3) + \delta_a(\text{CH}_3)$
2372	$\nu_a(\text{CH}_3) + \delta_s(\text{CH}_3)$	2261, 2213, 2208	$\nu(\text{Si-OH} \cdots \text{H}) + \delta(\text{Si-O-Si})$
2295	$\nu_a(\text{CH}_3) + \delta_a(\text{CH}_3)$	2184	$\nu(\text{Si-OH}) + \delta(\text{Si-O-Si})$
1851	$\nu_s(\text{CH}_3) + 2\delta_s(\text{CH}_3)$	2082	$\nu + \delta(\text{OH} \cdots \text{H})$, ethanol
1836	$\nu_a(\text{CH}_3) + 2\delta_s(\text{CH}_3)$	2060	$\nu + \delta(\text{OH})$, ethanol, less $\cdots \text{H}$ bonded
1784	$\nu_a(\text{CH}_3) + \delta_s(\text{CH}_3) + \delta_a(\text{CH}_3)$	1954, 1898, 1883	$\nu + \delta(\text{H}_2\text{O})$, $\cdots \text{H}$ bonded to Si-OH
1747	$\nu_s(\text{CH}_3) + 2\delta_a(\text{CH}_3)$, $2\nu_s(\text{CH}_3)$	1929	$\nu + \delta(\text{H}_2\text{O})$
1703, 1690	$2\nu_a(\text{CH}_3)$	1899, 1887	$\nu(\text{Si-OH}) + 2\delta(\text{Si-OH})$
1403	$\nu_s(\text{CH}_3) + 3\delta_a(\text{CH}_3)$	1758	$2\nu_s(\text{CH})$ in $-\text{CH}_3$
1374	$2\nu(\text{Si-OH})$, free SiOH	1713	$2\nu_a(\text{CH})$ in $-\text{CH}_2\text{-R}$
1185	$3\nu_s(\text{CH}_3)$	1697, 1684	$2\nu(\text{CH})$
1148	$3\nu_a(\text{CH}_3)$	1587	Broad band of ethanol
908	$4\nu_s(\text{CH}_3)$	1458, 1404	$2\nu(\text{H}_2\text{O})$
AMEO		1384	$2\nu(\text{Si-OH} \cdots \text{H}_2\text{O})$
2312	$\nu + \delta(\text{CH}_2)$	1367	$2\nu(\text{Si-OH})$, free Si-OH silica gel
2116	$\nu(\text{NH}_2) + \delta(\text{CH}_2)$	1200-1160	$3\nu(\text{C-H})$, in $-\text{CH}_3$, $-\text{CH}_2-$
2067	$\nu_s(\text{NH}_2) + \delta(\text{NH}_2)$	1174, 1146	$2\nu(\text{H}_2\text{O}) + \delta(\text{H}_2\text{O})$
2022	$\nu_a(\text{NH}_2) + \delta(\text{NH}_2)$	Sepiolite	
1724	$2\nu(\text{CH}_2)$	2422, 2387, 2313, 2292	$\nu + \delta(\text{OH})$ associated with cations (Al, Mg)
1530, 1486	$2\nu(\text{NH}_2)$	1925	$\nu + \delta(\text{H}_2\text{O})$, zeolitic water
Data from Workman, 2007; Bokobza et al., 2000; Cai et al., 2010; Christy, 2010; Frost et al., 2001; Mora et al., 2010; Ogasawara et al., 2000; Oikawa, 2000; Li Ou and Seddon, 1997.			

Although spectra were collected in reflectance mode, in what follows, they are presented using the second derivative, which allows a better visualization of the absorption bands. As a consequence of the transformation, these bands appear as positive peaks in the spectrum, but it should be mentioned that intensities are only

relative and are not directly correlated to the concentration of the corresponding compounds. Moreover, for most figures, only a few spectra covering the time range are displayed for clarity.

For the trial 1 spectra (Fig. 27), the added reference spectrum of pure TEOS (D40) shows in the 2200-2400 nm spectral range, absorption bands located at 2409, 2340, 2306 and 2264 nm, which can be attributed to combination modes ($\nu + \delta$) related to $-\text{CH}_2-$ and $-\text{CH}_3$ groups. At lower wavelengths, the absorption bands at 1770, 1732 and 1684 nm correspond to the first overtones of the C-H stretching involving the same groups while the second overtones appear at 1210, 1184 and 1142 nm. After 12 hours, these bands are already much less intense in comparison to those of pure TEOS, indicating that hydrolysis reactions are well advanced in accordance with the weight loss data. Until 566 hours, the intensity diminishes further, however, with small progressive shifts in the position of the bands towards shorter wavelengths for the combination bands while the first overtones follow an opposite trend (Fig. 27). Interestingly, for the 2340, 1770 and 1732 nm bands, this shift is combined with the appearance of absorption bands at 2298, 1784 and 1743 nm respectively (Fig. 27), which seem to progressively develop after about 92 hours and can be confidently attributed to $-\text{CH}_3$ absorptions of PDMS (Table 13). From these results, it can be inferred that a large part of the alkoxy groups in the TEOS reacted within the first 100 hours, which is again well-correlated with the weight loss data and curve profiles. Overall, these shifts reflect the compositional changes (Clark 1999) that result from the advancement of the hydrolysis reactions, after a few days leaving mainly absorptions associated with the organic component of the PDMS.

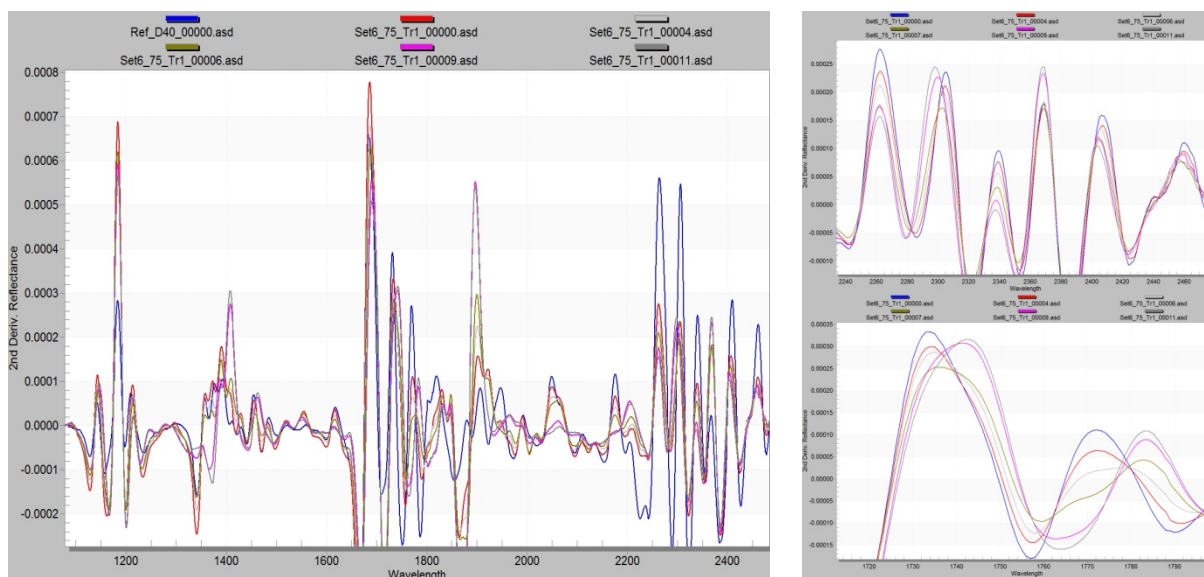


Fig. 27: Spectra of D40 and trial 1 with details of the band shifts occurring over time

While hydrolysis reactions progress releasing ethanol, condensation of the silanols also occurs, more intensively after 24 hours, as shown by the increase of the absorption band at 1900 nm characteristic of water (Fig. 28) though a contribution from silanol groups around this wavelength cannot be excluded (Table 13).

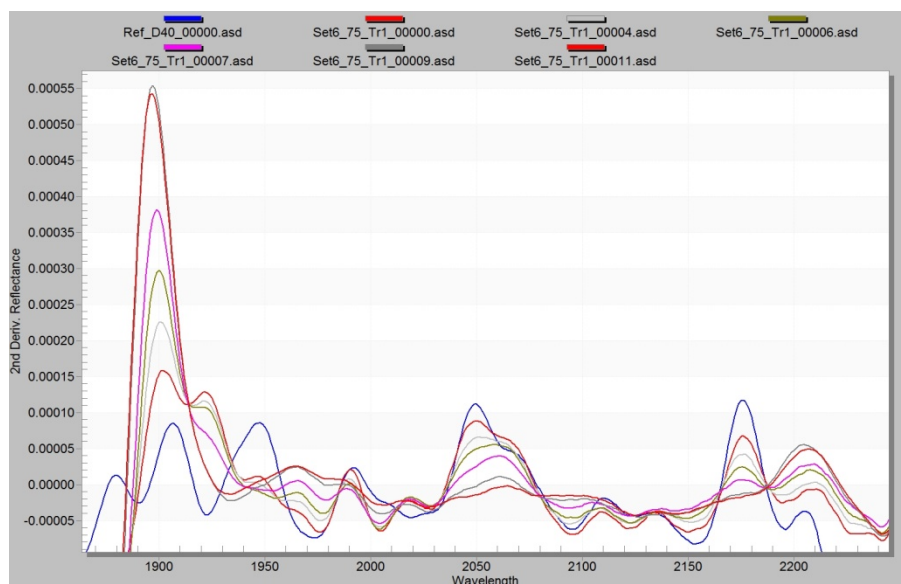


Fig. 28: Evolution of absorption bands in the 1870-2250 nm spectral range for trial 1 from 12 to 566 hours

Other absorption bands of less intensity also seem related to the sol-gel reactions, such as the ones at 2050-2070 nm, which show a steady decrease and could correspond to both combination modes of OH groups in ethanol and the ones at 2176 and 2205 nm, which could be attributed to Si-OH and Si-O-Si groups (Fig. 28). Similar contributions and changes, though more difficult to delineate, can also be observed in the first overtone region (OH) and would require further investigations for accurate attributions.

The influence of RH on the hydrolysis/condensation reactions was evaluated by comparing the spectra obtained at 75 and 25% at a given time (Fig. 29). It can be observed that the main difference is in the appearance and development of the absorption band at 1900 nm due to water (and maybe silanols). After 12 hours, spectra are similar with small differences related to the rate of the hydrolysis/condensation reactions. Over time however, the band at 1900 nm becomes more intense much earlier

(44 hours) for the trial at 75%, indicating that the condensation reactions have started, while for the trial at 25%, a significant increase occurs only later, between 284 and 566 hours. This confirms that the sol-gel transformation of TEOS takes place at a slower pace in dry conditions.

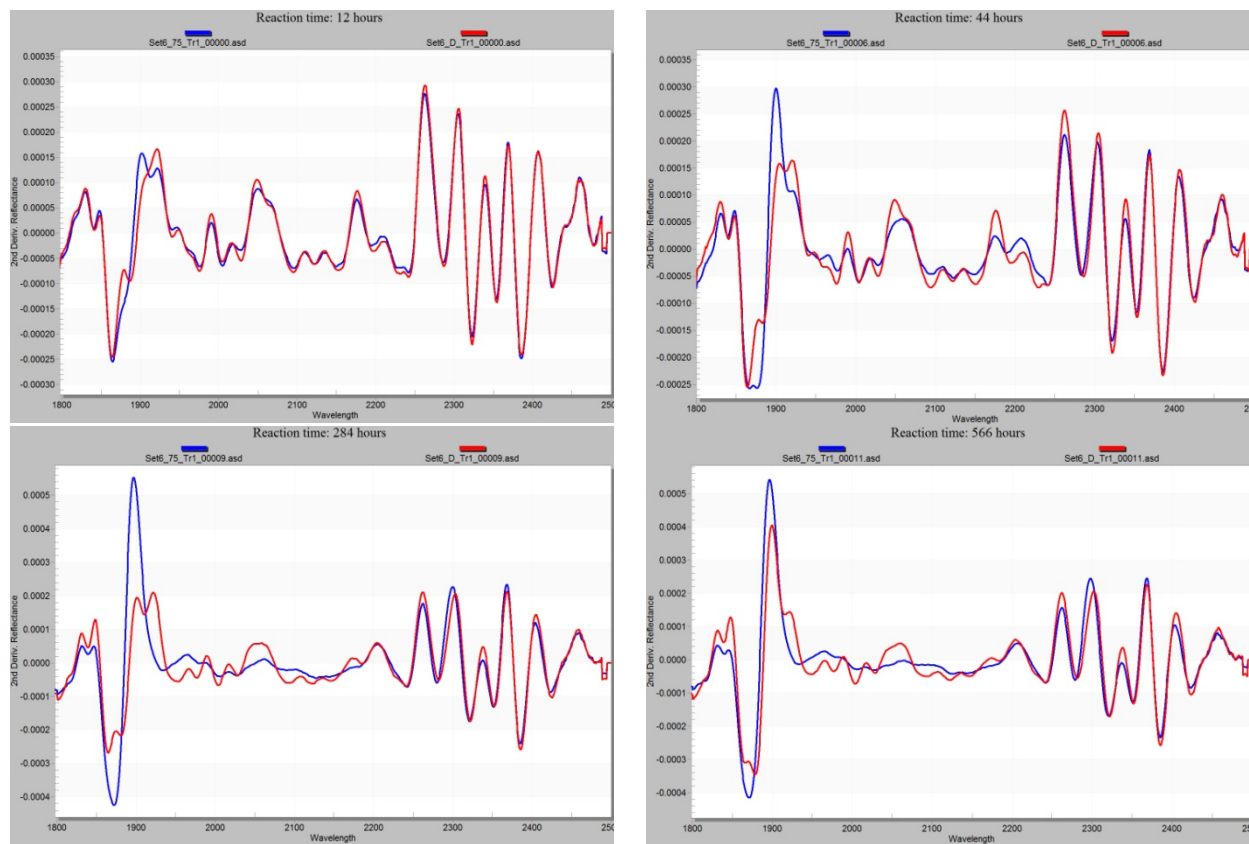


Fig. 29: Comparison between the spectra of trial 1 placed at 75 and 25% RH at various times (12, 44, 284 and 566 hours)

For the formulation with the AMEO silane (trial 9), spectra are similar to the ones discussed previously, however with additional bands due to the presence of AMEO. For the latter, the most prominent absorptions are due to the -NH_2 combination and first overtone modes with absorptions located at 2022 and around 1528 nm, respectively (Fig. 30). Contributions of the ethoxy groups cannot be distinguished from those of TEOS and the attribution of other absorption features were already discussed for Trial

1. One of the most noticeable changes over time is the important intensity decrease of the absorptions at 2263 and 2022/1528 nm. While the former reflects the fast hydrolysis rate of the alkoxy groups in TEOS and correlates well with weight loss and qualitative data, the latter is more difficult to explain as it relates to the 'non-reactive' amine group.

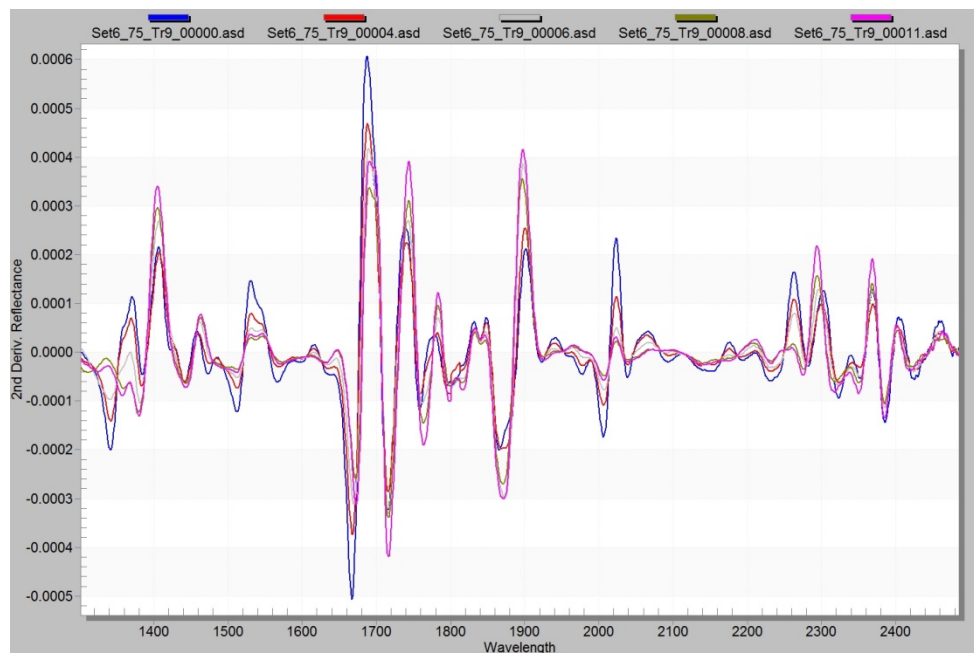


Fig. 30: Evolution of spectral signatures over time for the formulation with 2% AMEO (Trial 9).

However, the amine group can develop strong hydrogen bonds with silanols ($\text{Si-O}^- \cdots \text{H}_2\text{N}-$) or even get protonated ($\text{Si-O}^- \cdots {}^+\text{H}_3\text{N}-$), which could explain the intensity loss, but other possibilities such as a change in the diffraction/diffusion properties of the gel cannot be excluded. Another significant change is the intensity increase of the absorption around 1900 nm due to water molecules which to some extent reflects the progress of the condensation reactions as described previously for trial 1.

While the contribution of AMEO to accelerating the overall reaction rate when sufficient water is available is now well-established, this effect becomes much less visible in drier conditions where the system evolves similarly to a formulation without silane (Fig. 31) though interestingly, with almost identical water band intensities after 566 hours. Moreover, RH also seems to affect the behavior of the amine group, as at 25% RH the intensity of the band at 2020 nm is still strong while at 75%, this band has almost completely disappeared.

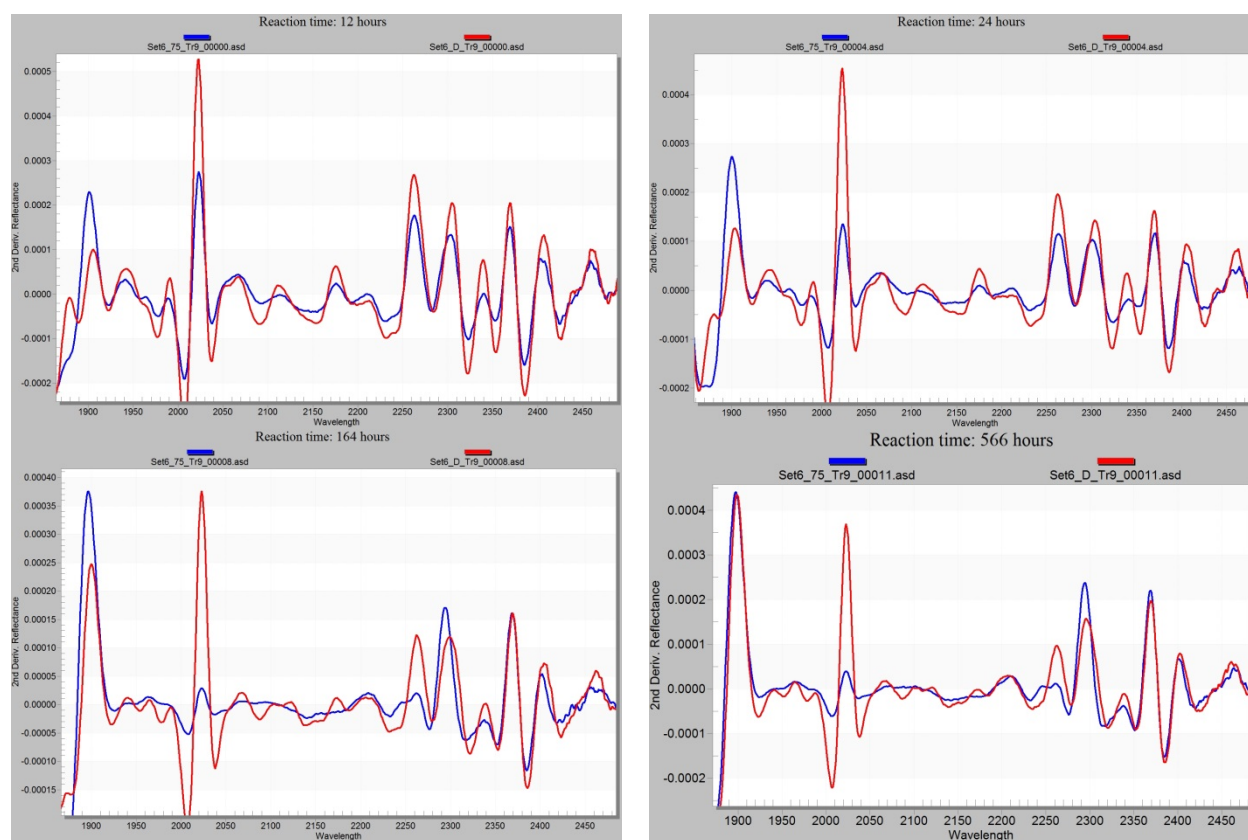


Fig. 31: Comparison between the spectra of trial 9 placed at 75 and 25% RH at various times (12, 24, 164 and 566 hours)

5.2.2. Dynamic mechanical analysis (DMA)

Table 14: Percent composition of samples used in DMA

TRIAL #	S:L	Composition					
		Solid			Liquid		
		M5	M40	B10	TEOS	PDMS	Silanes
							GLYMO
F-1	1:1	12.0	36.0	2.0	40.0	10.0	
F-2	1:1	12.0	36.0	2.0	30.0	20.0	
F-3	1:1	50.0			38.0	10.0	2.0
F-4	1:1	50.0			40.0	10.0	
LR-2	No solid				80.0	20.0	
LR-3	No solid				60.0	40.0	
LR-4	1:9			10.0	80.0	10.0	
R-75-2	No solid				80.0	20.0	
R-75-3	1:1	50.0			50.0		
R-75-4	1:9			10.0	90.0		
R-D-3	1:1	50.0			50.0		

For the trials tested (Table 14), the DMA results show that sample F-2 had the greatest tensile strength and toughness by far, though not the highest modulus (Fig. 32). A cluster of samples sits on the other end of the strength spectrum: L-R-2, L-R-3, and R-75-2, which have the lowest tensile strengths. It is expected that the L-R-2 and R-75-2 would have very similar results, as they have the exact same formulation and were kept under the same conditions. L-R-3, on the other, differed from the other two in formulation; while the other two have no solids content and 20% PDMS, L-R-3 contains 40% PDMS. Furthermore, the lower the percentage of PDMS for the rest of the trials, the higher the modulus; this implies that adding PDMS reduces the brittleness of the sample. The minor exception to this seems to be trial F-2, which contains 20% PDMS, but appears to have a slope closer to those with a 10% PDMS content. It is possible that the addition of sepiolite mitigates this affect, such that the combination of the 20%

PDMS content with a small amount of sepiolite provides additional strength, but may also detract somewhat from resistance to deformation.

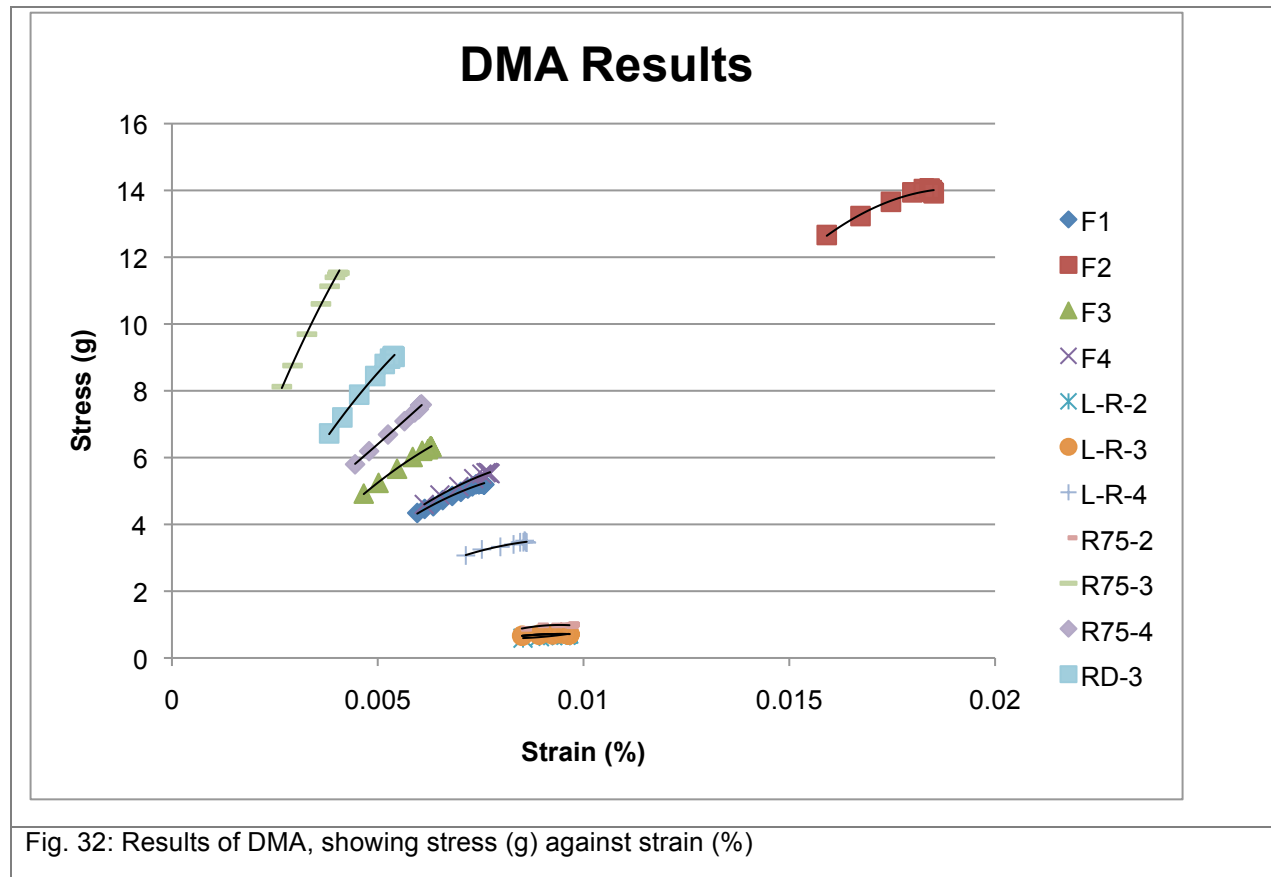


Fig. 32: Results of DMA, showing stress (g) against strain (%)

5.2.3. Scanning electron microscopy (SEM)

The surface morphology and microstructure varies considerably across samples. The topography in general appears to have larger, more jagged features (quartz grains) in high relief with surrounding microcracks for samples containing either M15 or M40 (2-6, 3-11, and 3-13) (Fig. 33). The degree of microcracking then may relate at least in part to the average particle diameter of the quartz, such that larger grains allow for a less cohesive grout. This may perhaps be mitigated with PDMS, as sample 2-6 shows a

smoother surface of polymer appearing next to a patch of more intense microcracks, which would be expected since the solid component is M40.

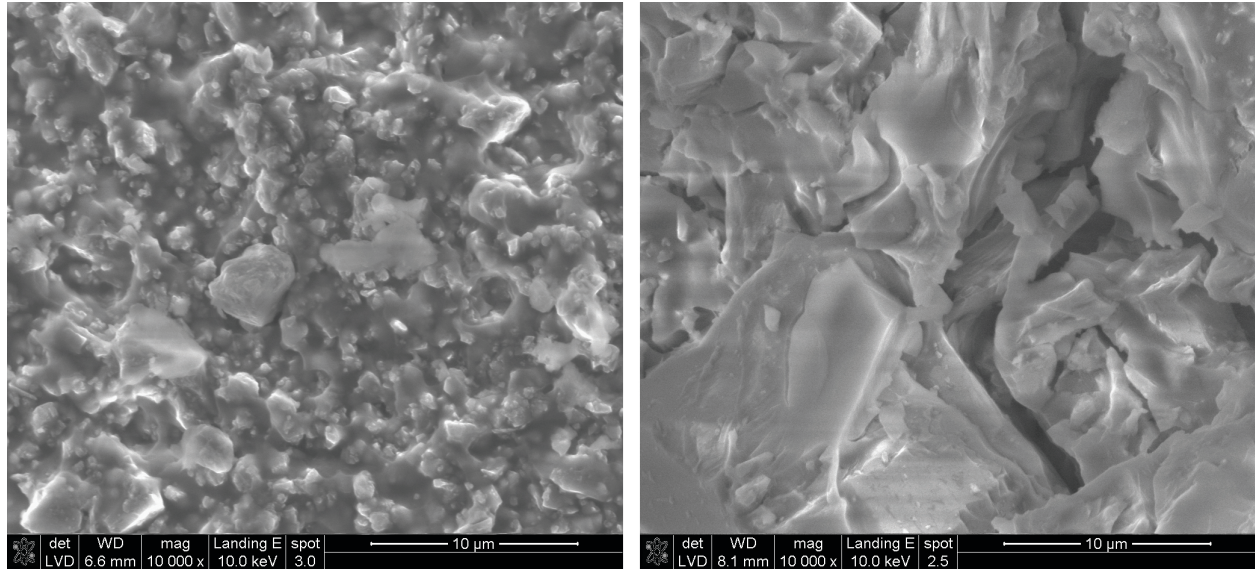


Fig. 33: The sample on the left (2-7) contains M5 quartz particles, while the sample on the right (3-11) contains M40. Microcracks are more visible in the image of 3-11, suggesting that particles of larger diameter may promote less cohesion within the grout.

In fact, higher concentrations of PDMS do appear to engender more bridging of quartz grains (1-10, 1-14, 2-6, and 2-7; 4-1 and 4-3) (Fig.34). In samples with more PDMS, a larger proportion of particles appear to be embedded in or covered by a homogeneous component with a smoother, polymeric surface. Sample 5-9 (fig. 35) shows where the polymer is more concentrated, with charge build-up; this contrasts with larger gray particles of sepiolite, probably coated with D40.

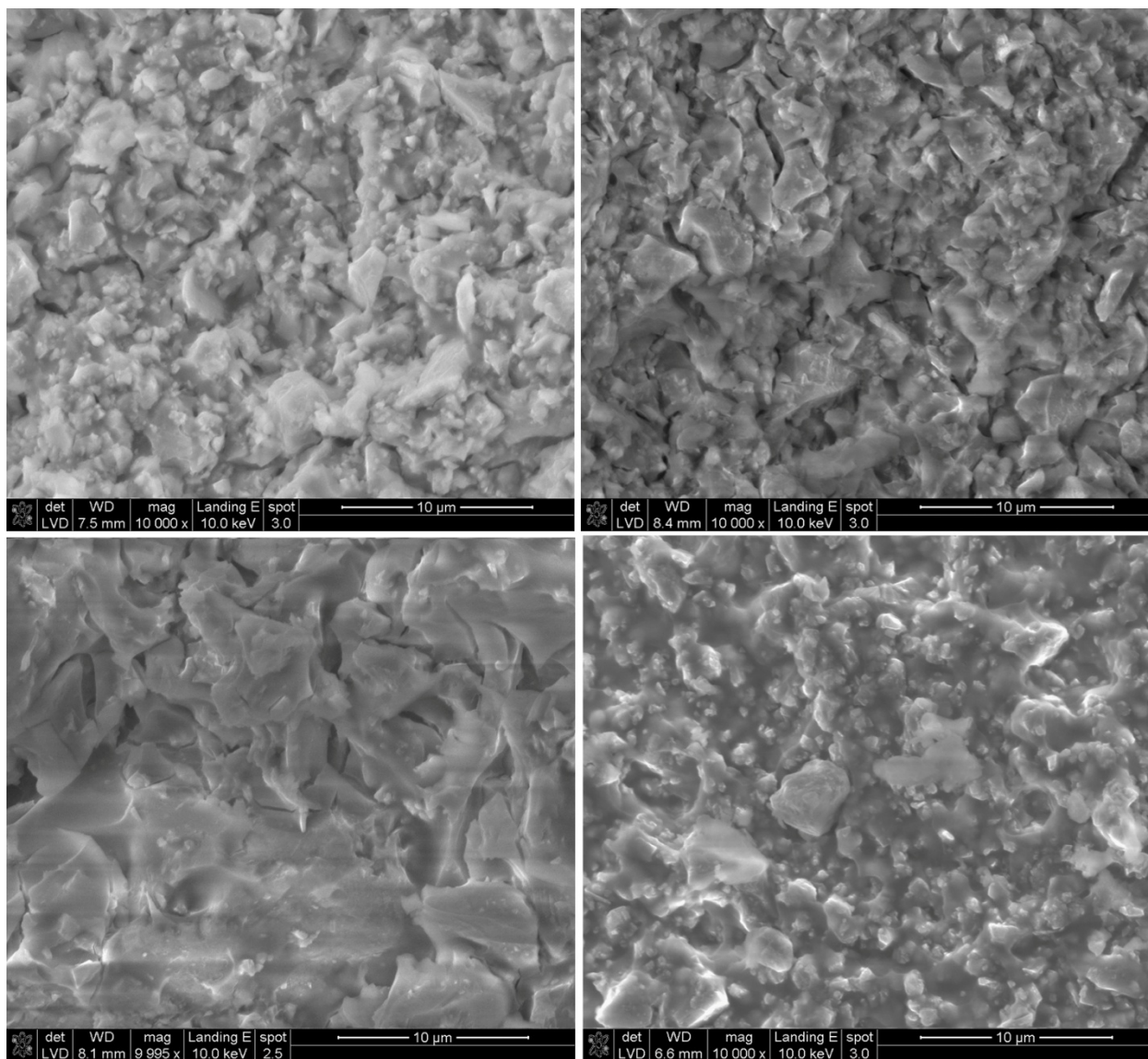


Fig. 34: At top left, Sample 1-10 has no PDMS content, while Sample 1-14 to the right has 2.5%. Below, Sample 2-6 contains larger particles (M40) and only 5% PDMS, while Sample 2-7 to the right contains smaller particles (M5) and 10% PDMS. Samples with a higher percentage of PDMS appear to show more bridging between grains.

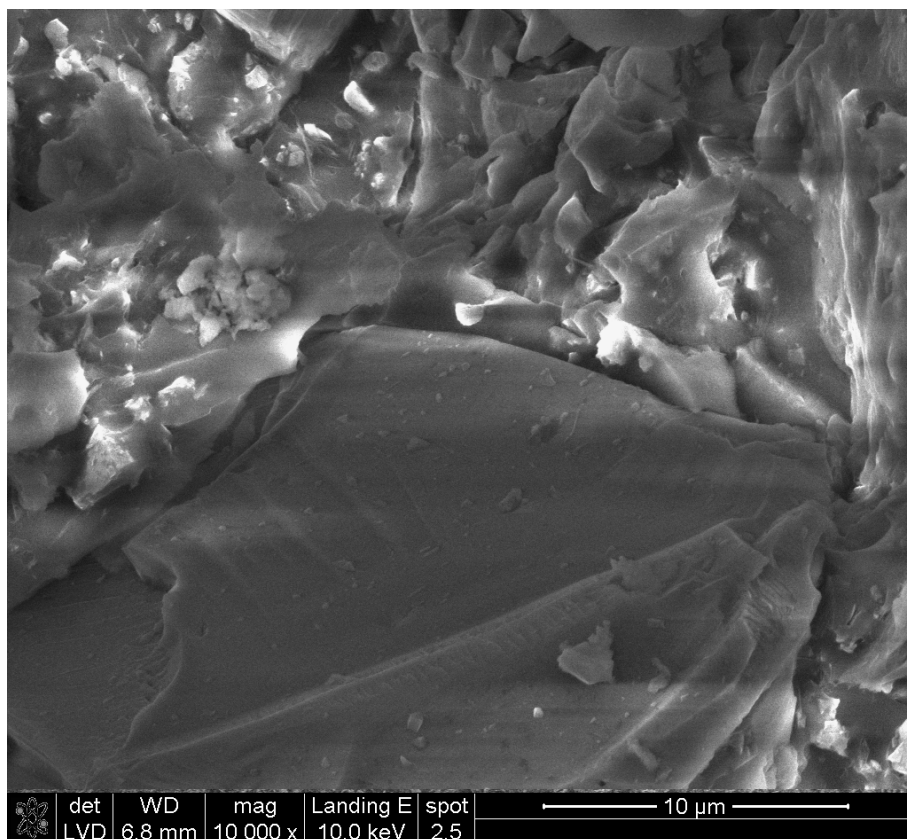


Fig. 35: Sample 5-9 shows a large gray area that is likely PDMS.

On the other hand, Samples 5-1 and 5-3 appear to show the opposite; however, interpretation must be reserved until the trials can be repeated. Meanwhile, sample 5-6 shows better bridging than 5-3 in spite of having the same amount of PDMS, and with a slightly higher percentage of B10.

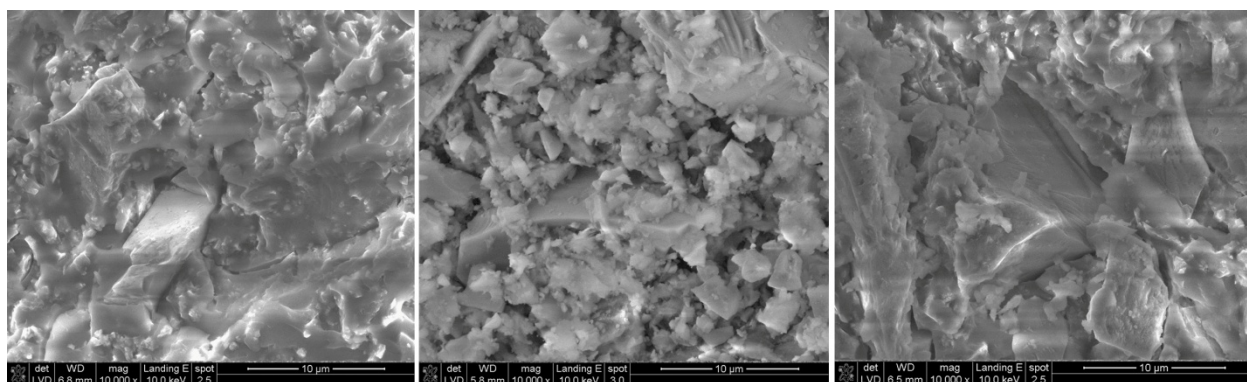


Fig. 36: Sample 5-1 on the left displays more bridging, despite having a lower concentration of PDMS than Sample 5-3 at the center. On the right, however, Sample 5-6 has the same amount of PDMS as Sample 5-3, and yet shows better bridging.

Finally, sample 5-11, which has a very high percentage of B10 (5%), but lower concentration of PDMS (10%), also shows excellent bridging of grains (fig. 37). From these examples, one possible conclusion is that it is not only the concentration of PDMS that improves bridging of grains, and thus cohesion, but its combined presence with sepiolite.

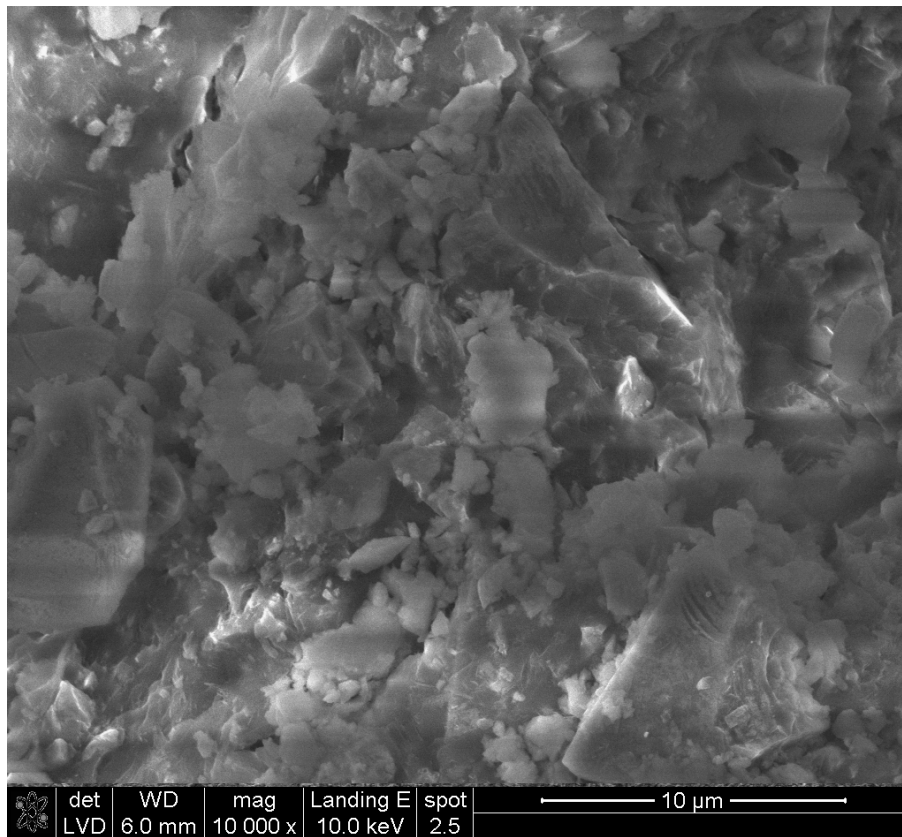


Fig. 37: Sample 5-11 shows extensive bridging of grains. Though it has a relatively lower concentration of PDMS (10%), it has a relatively high percentage of B10 sepiolite (5%).

A high concentration of B10 alone also seems to have an improved effect on the degree of microcracking and particle bridging. The only difference in formulation between Samples 5-3 and 5-6 is the amount of sepiolite (2% and 4%), and 5-6 appears to have more bridges, fewer microcracks, and a slightly more “coated” appearance (fig 36).

Interestingly, though samples with AMEO shattered at the macro level, microcracks were not detectable in the images of sample 4-4 (Fig. 37). Large cracks readily appear at 500x and 1000x. Perhaps the forces of adhesion are stronger than cohesion, causing rupture when the sample adhered to the side of the petri dish.

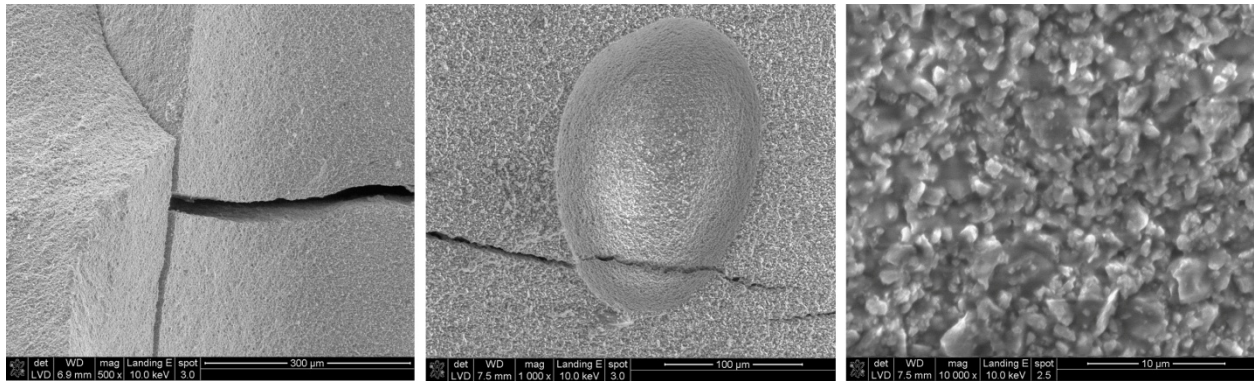


Fig. 38: Sample 4-4 is shown at 500x, 1000x, and 10000x, respectively. Though there are large cracks in the sample visible at less intense magnification and the macro level, there seem to be few microcracks visible.

6. Conclusion

These preliminary experimentation results show that ethyl silicate-based grouting formulations have much promise for application to porous weathered silicate stones characterized by low cohesion. Specifically, the relationship of concentration and reactivity of specific components was examined, and at both moderately high and low RH levels. First, the results indicate clearly that TEOS oligomers may provide a better alkoxysilane base than monomers, as the D40 trials showed less cracking. A mixture of crushed quartz varying in particle diameter gives the best results; however, workability of the initial mixtures was dependent on the complex relationship among the particle size, sepiolite, and PDMS. Larger particles tend to settle and resist suspension, though particles that were too small seemed to lack wettability, especially if the mixture included PDMS, and a sepiolite composition upwards of 5% severely reduced

workability. The numerous concentrations of PDMS tested show that it reduces cracking and shrinkage while adding flexibility, and a higher modulus, to the resulting gel. Furthermore, trials combining PDMS and sepiolite also displayed higher strength through reinforcement in general, and less cracking overall. The B10 sepiolite tended to increase viscosity enough to aid with suspension of larger quartz particles between 2-4% composition. The inclusion of AMEO in formulations had a negative effect in all examples due to its reactivity, which promotes shrinkage and cracking, while decreasing both strength and flexibility. Though GLYMO did not seem to have the same effect, further research is necessary to clarify its impact on the properties of both the sol and gel phases. Finally, at the very least, the relative humidity influences the evolution of the systems such that higher ambient humidity increases the rate of reaction. This is noteworthy especially for field applications, in which extreme high or low humidity may be uncontrollable.

However, these preliminary results would certainly benefit from further investigations, and experimentation could be improved given more time. A better system could be developed to quantitatively measure the shrinkage of the samples, rather than visual assessment; this would also necessitate the use of sample dishes of equal size. Following progress more closely to assess how different components may affect the rate of the reaction could be helpful for field testing, giving a better idea of working time. For example, a filmed time lapse was attempted for selected samples, but omitted due to project time constraints. Trials resulting in especially desirable properties should be repeated and examined more closely to ensure they are reproducible, and to provide a more in-depth assessment of results.

Most importantly, while this exploratory investigation identified a number of promising combinations in terms of desirable properties, formulations must be tested on weathered porous stone substrates to examine both short-term interactions and long-term aging properties. After this, only field testing can ensure ultimate compatibility with the substrate in a given environment, and overall suitability for conservation use.

Appendix A: List of Formulations by % Volume

TRIAL #	Solid:Liquid	SOLID					LIQUID				Mix Order	Workability	Separation	Shrinkage	Cracking	Strength	Flexibility
		Quartz			Sepiolite		TEOS	PDMS	Silanes								
		Minusil 5	Minusil 40	Others	B5	B10			AMEO	GLYMO							
LR-1	No solid						100.0					+	+	-	-	-	-
LR-2	No solid						80.0	20.0			D40 + PDMS-OH	+	++	+	+	++	+
LR-3	No solid						60.0	40.0			D40 + PDMS-OH	+	++	++	++	++	+++
LR-4	1:9					10.0	80.0	10.0			Liquids to solids	+	++	+	++	++	+
R-75-1	No solid						100.0					+	+	-	-	-	-
R-75-2	No solid						80.0	20.0			D40 + PDMS-OH	+	++	+	++	+	+++
R-75-3	1:1	50.0					50.0				Liquids to solids	+	++	-	+	++	+
R-75-4	1:9					10.0	90.0				Liquids to solids	+	++	-	++	++	+
R-75-5	1:9					DRIED 10.0	90.0				Liquids to solids	+	+	-	++	+++	+
R-D-1	No solid						100.0					+	++	+	+	+	+
R-D-2	No solid						80.0	20.0			D40 + PDMS-OH	+	++	+	+	+	+++
R-D-3	1:1	50.0					50.0				Liquids to solids	+	++	++	++	++	+
1-1							100.0 DA				Liquids to solids	+	++	-	-	+	+

1-2							100.0				Liquids to solids	+	++	-	-	-	-
1-3							95.0	5.0			Liquids to solids	+	++	-	+	+	+
1-4	3:2	60.0					40.0 DA				Liquids to solids	+	++	+	-	+	+
1-5	3:2		60.0				40.0 DA				Liquids to solids	+	-	++	+	-	-
1-6	3:2	60.0					40.0				Liquids to solids	+	++	+	++	+	+
1-7	3:2		60.0				40.0				Liquids to solids	+	-	+	+	++	+
1-8	1:1	50.0					50.0 DA				Liquids to solids	+	++	++	-	-	-
1-9	1:1		50.0				50.0 DA				Liquids to solids	+	+	+	-	-	-
1-10	1:1	50.0					50.0				Liquids to solids	+	++	-	++	++	+
1-11	1:1		50.0				50.0				Liquids to solids	+	-	+	-	+	+
1-12	3:2	60.0					38.0	2.0			Liquids to solids	+	++	-	+	++	++
1-13	3:2		60.0				38.0	2.0			Liquids to solids	+	-	-	-	+	+
1-14	1:1	50.0					47.5	2.5			Liquids to solids	+	++	+	++	++	+
1-15	1:1		50.0				47.5	2.5			Liquids to solids	+	-	+	-	+	+
2-1	3:2			60.0 M15			40.0				Liquids to solids	+	-	+	+	++	-
2-2	1:1			50.0 M15			50.0				Liquids to solids	+	-	-	+	++	+
2-3	3:2			60.0 M15			38.0	2.0			Liquids to solids	+	-	-	+	+++	+
2-4	1:1			50.0 M15			47.5	2.5			Liquids to solids	+	-	-	+	+++	+
2-5	1:1	50.0					45.0	5.0			Liquids to solids	+	++	-	+	+++	+
2-6	1:1		50.0				45.0	5.0			Liquids to solids	+	-	-	-	+	+
2-7	1:1	50.0					40.0	10.0			Liquids to solids	+	++	-	+	+++	+
2-8	1:1		50.0				40.0	10.0			Liquids to solids	+	-	-	-	+	+
2-9												+					
2-10												+					
2-11	1:1	50.0					47.5	2.5			Solids to liquids	+	++	-	+	++	+
2-12	1:1	50.0					47.5	2.5			Liquids to solids	+	++	-	++	+++	+
3-1	3:2		59.0		1.0		40.0				Liquids to solids	+	+	++	++	+	-
3-2	1:1		49.0		1.0		50.0				Liquids to solids	+	-	-	+	+	-
3-3	3:2			59.0 M15	1.0		40.0				Liquids to solids	+	+	+	+	++	+
3-4	3:2		59.0			1.0	40.0				Liquids to solids	+	+	+	+	+	-
3-5	1:1		49.0			1.0	50.0				Liquids to solids	+	-	+	+	+	-

3-6	3:2			59.0 M15		1.0	40.0				Liquids to solids	+	+	-	+	++	+
3-15	3:2		59.5		0.5		40.0				Liquids to solids	+	-	+	++	+	-
3-16	1:1		49.5		0.5		50.0				Liquids to solids	+	-	-	-	+	-
3-17	3:2			59.5 M15	0.5		40.0				Liquids to solids	+	+	+	++	++	-
3-18	3:2		59.5			0.5	40.0				Liquids to solids	+	+	+	++	+	-
3-19	1:1		49.5			0.5	50.0				Liquids to solids	+	+	-	+	+	-
3-20	3:2			59.5 M15		0.5	40.0				Liquids to solids	+	++	-	+	++	-
3-7	3:2		59.0		1.0		38.0	2.0			Liquids to solids	+	-	+	+	+	-
3-8	1:1		49.0		1.0		47.5	2.5			Liquids to solids	+	-	+	+	+	-
3-9	3:2			59.0 M15	1.0		38.0	2.0			Liquids to solids	+	+	+	++	++	+
3-10	1:1		49.0		1.0		45.0	5.0			Liquids to solids	+	-	-	-	+	-
3-11	3:2		59.0			1.0	38.0	2.0			Liquids to solids	+	-	+	+	+	-
3-12	1:1		49.0			1.0	47.5	2.5			Liquids to solids	+	-	-	-	+	-
3-13	3:2			59.0 M15		1.0	38.0	2.0			Liquids to solids	+	++	+	+++	++	++
3-14	1:1		49.0			1.0	45.0	5.0			Liquids to solids	+	-	-	+	+	-
4-1	1:1	49.0				1.0	50.0				Liquids to solids	+	++	+	++	++	+
4-2	1:1	49.0				1.0	45.0	5.0			Liquids to solids	-	++	+	++	++	+
4-3	1:1	49.0				1.0	40.0	10.0			Liquids to solids	+	++	-	++	+++	+
4-4	1:1	49.0				1.0	44.0	5.0	1.0		Liquids to solids	+	++	-	-	-	-
4-5	1:1	49.0				1.0	44.0	5.0		1.0	Liquids to solids	+	++	+	++	+++	+
4-6	1:1	23.5	23.5			3.0	50.0				Liquids to solids	+	++	-	+	++	+
4-7	1:1	23.5	23.5			3.0	45.0	5.0			Liquids to solids	+	++	-	+	++	+
4-8	1:1	23.5	23.5			3.0	40.0	10.0			Liquids to solids	+	++	+	+++	++	+
4-9	1:1	47.0				3.0	50.0				Liquids to solids	+	++	-	+	+	+
4-10	1:1	47.0				3.0	45.0	5.0			Liquids to solids	+	++	-	+	++	+
4-11	1:1	47.0				3.0	40.0	10.0			Liquids to solids	+	++	+	+++	++	+
4-12	1:1	47.0				3.0	30.0	20.0			Liquids to solids	+	++	++	+++	++	+++
5-1	1:1	24.0	24.0			2.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	+	+++	+++	++
5-2	1:1	24.0	24.0			2.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	+	+++	++	++

5-3	1:1	24.0	24.0			2.0	20.0	30.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	++	+++
5-4	1:1	23.0	23.0			4.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	-	++	-	++	+++	++
5-5	1:1	23.0	23.0			4.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	++	++
5-6	1:1	23.0	23.0			4.0	20.0	30.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	++	+++
5-7	1:1	9.6	38.4			2.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+	+	+	++	++	++
5-8	1:1	9.6	38.4			2.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	+++	++
5-9	1:1	9.4	37.6			3.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	+	++	+++	++
5-10	1:1	9.4	37.6			3.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	+++	++
5-11	1:1	9.0	36.0			5.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	-	++	+	+++	++	++
5-12	1:1	9.0	36.0			5.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	-	++	+	+++	++	++
5-13	1:1	9.6	38.4			2.0	36.0	10.0	4.0		M5 + D40 + B10 + M40 + PDMS-OH + Silane	+	++	-	-	-	-
5-14	1:1	9.6	38.4			2.0	36.0	10.0		4.0	M5 + D40 + B10 + M40 + PDMS-OH + Silane	+	++	+	+++	++	++
5-15	1:1	9.6	38.4			2.0	32.0	10.0	8.0		M5 + D40 + B10 + M40 + PDMS-OH + Silane	+	++	-	-	-	-
5-16	1:1	9.6	38.4			2.0	32.0	10.0		8.0	M5 + D40 + B10 + M40 + PDMS-OH + Silane	+	++	+	++	++	++

5-17	1:1	9.4	37.6			3.0	40.0	10.0		M5 + PDMS-OH + D40 + B10 + M40	+	++	+	+++	+++	++
6-75-1	1:1	24.0	24.0			2.0	40.0	10.0		M5 + D40 + B10 + M40 + PDMS-OH	+	+	-	++	++	++
6-75-2	1:1	24.0	24.0			2.0	30.0	20.0		M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	++	+++
6-75-3	1:1	12.0	36.0			2.0	40.0	10.0		M5 + D40 + B10 + M40 + PDMS-OH	+	+	+	++	++	++
6-75-4	1:1	12.0	36.0			2.0	30.0	20.0		M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	++	++
6-75-5	1:1		48.0			2.0	40.0	10.0		M40 + D40 + B10 + PDMS-OH	+	+	-	++	+	+
6-75-6	1:1	12.0		36.0 Sil 75		2.0	40.0	10.0		M5 + D40 + B10 + Sil75 + PDMS-OH	+	+	+	++	-	-
6-75-7	1:1	12.0		36.0 GS-40		2.0	40.0	10.0		M5 + D40 + B10 + GS-40 + PDMS-OH	+	-	-	-	-	+
6-75-8	1:1	10.0		34.0 GS-40		4.0	40.0	10.0		M5 + D40 + B10 + GS-40 + PDMS-OH	+	-	-	-	-	+
6-75-9	1:1	50.0					38.0	10.0	2.0	M5 + D40 + PDMS-OH + silane	+	+	-	-	+++	++
6-75-10	1:1	50.0					38.0	10.0	2.0	M5 + D40 + PDMS-OH + silane	+	++	+	++	-	-
6-75-11	1:1						88.0	10.0	2.0	D40 + PDMS-OH + silane	+	++	-	-	+	+
6-75-12	1:1	12.0		36.0 Vol. HGS		2.0	40.0	10.0		M5 + D40 + B10 + HGS + PDMS-OH	+	++	-	+	+	++
6-75-13	1:1			50.0 Vol. HGS			40.0	10.0		D40 + HGS + PDMS-OH	+	-	-	+	+++	++
6-75-14	1:19					5.0	85.0	10.0		B10 + D40 + PDMS-OH	+	-	-	+	++	+++

6-25-1	1:1	24.0	24.0			2.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+	-	+	++	++	++
6-25-2	1:1	24.0	24.0			2.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	++	+++	+	+++
6-25-3	1:1	12.0	36.0			2.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+	+	+	++	+	+
6-25-4	1:1	12.0	36.0			2.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+	++	+	+++	++	+
6-25-5	1:1		48.0			2.0	40.0	10.0			M40 + D40 + B10 + PDMS- OH	+	+	-	++	+	++
6-25-6	1:1	12.0		36.0 Sil 75		2.0	40.0	10.0			M5 + D40 + B10 + Sil75 + PDMS-OH	+	+	-	+	++	+
6-25-7	1:1	12.0		36.0 GS- 40		2.0	40.0	10.0			M5 + D40 + B10 + GS-40 + PDMS-OH	+	-	-	-	-	+
6-25-8	1:1	10.0		34.0 GS- 40		4.0	40.0	10.0			M5 + D40 + B10 + GS-40 + PDMS-OH	+	+	-	+	-	+
6-25-9	1:1	50.0					38.0	10.0	2.0		M5 + D40 + PDMS-OH + silane	+	-	+	+	+	+
6-25-10	1:1	50.0					38.0	10.0		2.0	M5 + D40 + PDMS-OH + silane	+	++	+	++	+++	++
6-25-11	1:1						88.0	10.0	2.0		D40 + PDMS- OH + silane	+	++	-	-	-	-
6-25-12	1:1	12.0		36.0 Vol. HGS		2.0	40.0	10.0			M5 + D40 + B10 + HGS + PDMS-OH	+	++	-	-	+	+
6-25-13	1:1			50.0 Vol. HGS			40.0	10.0			D40 + HGS + PDMS-OH	+	-	-	-	-	-
6-25-14	1:19					5.0	85.0	10.0			B10 + D40 + PDMS-OH	+	-	-	+	++	-
F-1	1:1	12.0	36.0			2.0	40.0	10.0			M5 + D40 + B10 + M40 + PDMS-OH	+					

F-2	1:1	12.0	36.0			2.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+					
F-3	1:1	50.0					38.0	10.0		2.0	M5 + D40 + PDMS-OH + silane	+					
F-4	1:1	50.0					40.0	10.0			M5 + D40 + PDMS-OH + silane	+					
F-5	1:1	9.4	37.6			3.0	30.0	20.0			M5 + D40 + B10 + M40 + PDMS-OH	+					

Bibliography

Aggelakopoulou E., Charles P., Acerra M.E., Garcia A.I., Flatt, R.J. and Scherer G.W. 2002. "Rheology Optimization of Particle Modified Consolidants" *Symposium II – Materials Issues in Art and Archaeology VI.12*: 15–20.

Anson Cartwright T., and Vergès-Belmin V. 2008. "ICOMOC-ISCS Illustrated Glossary on Stone Deterioration Patterns." Paris: ICOMOS International Scientific Committee for Stone.

Bokobza, L. 2004. "Elastomeric Composites. I. Silicone Composites." *Journal of Applied Polymer Science* 93 (5): 2095–2104.

Bokobza L., Buffeteau T. and Desbat B., 2000. "Mid- and Near-Infrared Investigation of Molecular Orientation in Elastomeric Networks." *Applied Spectroscopy*, 54, 3, 360-365.

Cai D., Neyer A., Kuckuk R. and Heise H.M., 2010. "Raman, mid-infrared, near-infrared and ultraviolet–visible spectroscopy of PDMS silicone rubber for characterization of polymer optical waveguide materials." *Journal of Molecular Structure*, 976, 274-281.

Charola, A.E., and Koestler R.J. 1986. "Scanning Electron Microscopy in the Evaluation of Consolidation Treatments for Stone." *Scanning Electron Microscopy* 1986 (2): 479–84.

Chaudhry, Charu. 2007. "Evaluation of Grouting as a Strengthening Technique for Earthen Structures in Seismic Areas: Case Study Chiripa". University of Pennsylvania.

Christy A.A. 2010. "New insights into the surface functionalities and adsorption evolution of water molecules on silica gel surface: A study by second derivative near infrared spectroscopy." *Vibrational Spectroscopy*, 54, 42-49.

Clifton, J.R. 1980. "Stone Consolidating Materials: A Status Report". Accessed January 21, 2014. <http://cool.conservation-us.org/byauth/clifton/stone/>.

De Witte, E., Charola A.E., and Sherry R.P. 1985. "Preliminary Tests on Commercial Stone Consolidants." In *5th International Congress on the Deterioration and Conservation of Stone, Lausanne, 1985*, 709–18. Presses Polytechniques Romandes, Lausanne.

Doehne, E., and Price C.A. 2010. *Stone Conservation: An Overview of Current Research*. Second edition. Los Angeles: Getty Conservation Institute.

Escalante, M.R., Valenza J., and Scherer G.W. 2000. "Compatible Consolidants from Particle-Modified Gels." In *Proceedings of the 9th International Congress on the Deterioration and Conservation of Stone*, 2:459–65. Amsterdam: Elsevier.

Frost R.L., Locos O.B., Ruan H. and Klopogge J.T., 2001. "Near-infrared and mid-infrared spectroscopic study of sepiolites and palygorskites." *Vibrational Spectroscopy*, 27, 1-13.

Goins, E.S. 1995. "Alkoxysilane stone consolidants: The effect of the stone substrate on the polymerization process." University College London, University of London.

Grissom, C.A. 1994. "The Deterioration and Treatment of Volcanic Stone: A Review of the Literature." *Lavas and Volcanic Tuffs: Proceedings of the International Meeting, Easter Island, Chile, 25-31 October, 1990*. Rome: International Centre for the Study of the Preservation and the Restoration of Cultural Property.

Houlsby, A.C. 1990. *Construction and Design of Cement Grouting: A Guide to Grouting in Rock Foundations*. John Wiley & Sons.

Jones, J.R. 2012. "Sol-Gel Derived Glasses for Medicine." In *Bio-Glasses*, edited by J. R. Jones and A. G. Clare, 29–44. John Wiley & Sons, Ltd.

Kalagri, A., Miltiadou-Fezans A., Vintzileou E. 2010. "Design and evaluation of hydraulic lime grouts for the strengthening of stone masonry historic structures." *Materials and Structures*. 43 (8), 1135-1146.

Laurenzi Tabasso, M., Mecchi A.M., and Santamaria U. 1994. "Interaction between Volcanic Tuff and Products Used for Consolidation and Waterproofing Treatments": 173–90.

Li Ou D. and Seddon A.B., 1997. "Near- and mid-infrared spectroscopy of sol-gel derived ormosils: vinyl and phenyl silicates." *Journal of Non-Crystalline Solids*, 210, 187-203.

Li, X., Wang Q., Li H., Ji H., Sun X., and He J. 2013. "Effect of Sepiolite Fiber on the Structure and Properties of the Sepiolite/silica Aerogel Composite." *Journal of Sol-Gel Science and Technology* 67 (3). 646 – 653.

Mackenzie, J.D., and Bescher E.P. 1998. "Structures, Properties and Potential Applications of Ormosils." *Journal of Sol-Gel Science and Technology* 13 (1-3): 371–77.

Maish, J.P. 1994. "Silicone Rubber Staining of Terracotta Surfaces." *Studies in Conservation* 39 (4): 250–56.

McIntosh, L. 2007. "Ethyl Silicate as an Alternative Binder for Grout and Mortar for Use with American Sandstones." Columbia University.

Méndez-Vivar, J. 2006. "The Interaction of Dibutyltin Dilaureate with Tetraethyl Orthosilicate in Sol-Gel Systems." *Journal of Sol-Gel Science and Technology* 38 (2): 159 – 166.

Miliani, C., Velo-Simpson, M.L. and Scherer G.W. 2007. "Particle-Modified Consolidants: A Study on the Effect of Particles on Sol-gel Properties and Consolidation Effectiveness." *Journal of Cultural Heritage* 8 (1): 1–6.

Mora M., López I.M., Carmona Á.M., Jiménez-Sanchidrián C. and Ruiz R.J., 2010. "Study of the thermal decomposition of a sepiolite by mid- and near-infrared spectroscopies." *Polyhedron*, 29, 3046-51.

Mosquera, M. J., de los Santos D.M., Montes A., and Valdez-Castro L. 2008. "New Nanomaterials for Consolidating Stone." *Langmuir: The ACS Journal of Surfaces and Colloids* 24 (6): 2772–78.

Ogasawara T., Nara A., Okabayashi H., Nishio E. and O'Connor C.J., 2000. "Time-resolved near-infrared and two-dimensional near-infrared correlation spectroscopic studies of the polymerization process of silane coupling agents. Dynamic behavior of water molecules in the 3-aminopropyl-triethoxysilane-ethanol-water system." *Colloid Polym Sci*, 278, 1070-84.

Oikawa N., 2000. "Near-Infrared Spectroscopic Study for the Sol-Gel Reaction using Alkoxysilanes." *Journal of Sol-Gel Science and Technology*, 19, 729-732.

Pingarrón Alvarez, V. 2006. "Performance Analysis of Hydraulic Lime Grouts for Masonry Repair." Accessed May 15, 2012. http://repository.upenn.edu/hp_theses/13.

Rousset, B., Gentile S., James J., and Pozzi B. 2005. "Injection Grouts for Molasse Sandstones: Preliminary Assessments." In *Repair Mortars for Historic Masonry*. Delft University of Technology, Delft, the Netherlands.

Salazar-Hernández, C., Alquiza M. J. P., Salgado P., and Cervantes J. 2010. "TEOS–colloidal silica–PDMS-OH Hybrid Formulation Used for Stone Consolidation." *Applied Organometallic Chemistry* 24 (6): 481–88.

Scherer, G. W., and Wheeler G.S. 2009. "Silicate Consolidants for Stone." *Key Engineering Materials* 391: 1–25.

Shirosaki, Y., Osaka A., Tsuru K., and Hayakawa S.. 2012. "Inorganic-Organic Sol-Gel Hybrids." In *Bio-Glasses*, edited by Julian R. Jones and Alexis G. Clare, 139–58. John Wiley & Sons, Ltd.

Tartaglione, G., Tabuani D., and Camino G. 2008. "Thermal and Morphological Characterisation of Organically Modified Sepiolite." *Microporous and Mesoporous Materials* 107 (1–2): 161–68.

Torraca, G. 1988. "General philosophy of stone conservation." *The Deterioration and Conservation of Stone: Notes from the International Venetian Courses on Stone Restoration*. Venice: UNESCO.

Useche, L. A. 1994. "Studies for the Consolidation of the Facade of the Church of Santo Domingo, Popayan, Colombia." *Lavas and Volcanic Tuffs: Proceedings of the International Meeting, Easter Island, Chile, 25-31 October, 1990*. Rome: International Centre for the Study of the Preservation and the Restoration of Cultural Property.

Warren, J. 1999. *Conservation of Earth Structures*. Oxford, England: Butterworth-Heinemann.

Wheeler, G. 2005. *Alkoxysilanes and the Consolidation of Stone*. 1st ed. Los Angeles: Getty Conservation Institute.

Wong, K. H. 2006. "Assessment of the Grout Used for the Structural Stabilization of the Early Phrygian Citadel Gate at Gordion, Turkey". University of Pennsylvania.

Workman J., 2007. *Practical Guide to Interpretive Near-Infrared Spectroscopy*. J. Workman and L. Weyer eds., CRC Press, New York.

Zárraga, R., Cervantes J., Salazar-Hernandez C., and Wheeler G. 2010. "Effect of the Addition of Hydroxyl-Terminated Polydimethylsiloxane to TEOS-Based Stone Consolidants." *Journal of Cultural Heritage* 11 (2): 138–44.