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Effect of modified ethylsilicate consolidants on the mechanical properties of sandstone

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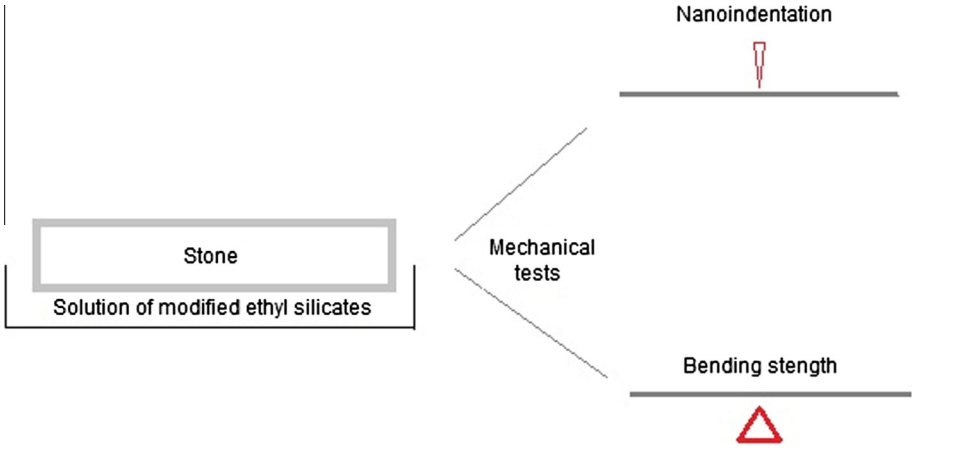
HIGHLIGHTS

- Tailoring ethylsilicate consolidant properties by particles and forming mesoporosity.
- Removal of the excessive surface consolidation.
- Increase in the hardness and Young's modulus of consolidant gel due to particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon alkoxides, such as silicon ethoxide or its oligomers (generally called ethylsilicates), are excellent consolidants for the weathered silicate materials. Their drawbacks, the shrinkage and cracking, can be reduced by the formation of wider pores within the gels or by the modification with particles. The sol-gel process was found to depend on the properties of particles added, especially on their size and surface properties. While the hydrophobization of the particle surface decelerated the process, the adding of hydroxylated particles had only a slight effect on the polycondensation process. In order to suppress the formation of micropores and to support the formation of more advantageous, substantially wider mesopores, organic amines are preferable as catalysts. The role of primary amines with a longer alkyl chain seems more complex than that of mere catalysts. If particles were added, no substantial effect on the character of the porosity was observed. The mechanical properties of gels modified by embedding particles or by creating mesoporosity were substantially changed. Due to the embedding of particles both the hardness and Young's modulus were increased. On the other hand, the formation of the mesoporosity within the gels had an opposite effect. The modification of consolidants by the creation of mesopores in the gels enabled to achieve an even consolidation of the stone characterized by moderate strength changes due to consolidating treatment. On the contrary, the variants with particles exhibited much higher strength increase in the surface part of stone specimens compared to inner or bottom stone areas, which is not suitable for a satisfactory consolidating intervention.

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1. Introduction

Silicon alkoxides, such as silicon ethoxide or its oligomers (generally called ethylsilicates), are excellent consolidants for the weathered silicate materials [1]. However, they suffer from two major drawbacks. First, the shrinkage and cracking of the formed gels due to the syneresis and residual drying stress lead to their decreased mechanical strength [2]. Due to their compact microporous texture (pores narrower than 2 nm), the capillary pressure, which is reciprocally proportional to the pore width according to the Young-Laplace equation, is very high, what the relatively brittle framework of the siliceous gel cannot withstand [3,4]. Second, the physical properties of the gel phase do not match those of the treated stone (such as the dynamic elastic modulus, hardness, thermal expansion coefficient, porosity etc.).

The shrinkage and cracking of the gel can be reduced by the formation of wider pores within the gels [5–7] or by the modification with particles [8,9]. We have found that the shrinkage and cracking of the gel films due to drying is drastically reduced because of the presence of incorporated nanoparticles smaller than about 10–20 nm and the formation of mesopores about 10 nm in width. We have recently developed a novel preparation strategy called "brick and mortar" based on the fusion of preformed nanocrystals with surfactant-templated sol-gel material, which acts as a structure-directing matrix and as a chemical glue [10–12]. We have found that this technique is not only suitable for the preparation of thin layers for the application in solar cells, photocatalysis or sensors, but also enables to obtain consolidants with very promising properties.

The modification of gels can be expected to have a substantial effect on their physico-chemical and especially mechanical properties, depending on the properties of particles (e.g., their size and the nature of their surface), and the character of porosity created. It can be anticipated that the characteristics of the modified gels containing embedded particles and wider pores will be closer to those of the consolidated stone than the properties of purely polymeric gels.

This communication aims at the determination and analysis of the effect of the addition of particles and formation of pores on the elastic modulus and hardness of the gels formed either without space restrictions in a Petri dish or within the pores of sandstone. Elastic modulus and hardness of the sandstone specimen are obtained from load-displacement measurements in nanoindentation tests. In these tests, the depth of penetration beneath the specimen surface is measured as the load is applied to the indenter. By this technique also the distribution of the consolidant applied on the sandstone sample can be determined. Nanoindentation is a versatile method for material characterization at scales where classical mechanical tests are inadequate. Additionally the effect of the consolidation of sandstones with modified gels on their bending strength was determined.

2. Materials and methods

2.1. Preparation of modified ethylsilicate consolidants

Chemicals used include Dynasylan 40 (Evonik), di-n-butyltin dilaurate (Alfa Aesar), isopropanol (Lach Ner), 1-octylamine (Alfa Aesar), 1-dodecylamine (Fluka), 1-hexadecylamin (Aldrich). Particles of silicon dioxide were obtained from Evonik and Cabot, including pristine hydrophilic particles 13.5 nm in size and hydrophobized ones either methylated or octylated 24 nm and 18 nm in size, respectively. The particle size given was provided by the corresponding producers. However, these primary nanoparticles tend to cluster forming aggregates several hundreds of nanometers in size. Adsorption measurement using nitrogen as adsorptive showed the aggregates consisted of a lose, unconsolidated assemblage of primary nanoparticles. The particle size distribution of aggregates of hydrophilic nanoparticles exhibited a maximum at ca 375 nm without any marked change even after the storage time of eighteen months. There was a very small percentage of particle aggregates larger than ca 800 nm.

The gels were prepared from Dynasylan 40, which is a mixture of monomeric and oligomeric ethoxysilanes, the average chain length being about five Si–O units. First a suspension of particles and catalyst in isopropanol was prepared. Particles were added at the concentration of 5%. As a catalyst, either dibutyltin dilaurate (DBTDL) or organic amines at the concentrations of 1% and 0.4%, respectively, were used. Second Dynasylan 40 was diluted with isopropanol at the ratio of 1:1 (v/v). Finally the diluted Dynasylan solution was added to the suspension of particles and catalysts in isopropanol. After 24 h the sol was suitable for the application. An overview of samples prepared is given in Table 1.

The samples prepared were designated as follows (see Table 1): D, from pristine Dynasylan 40 with DBTDL as catalyst, DA, modified with hydrophilic particles, DBTDL as catalyst, DTS, modified with hydrophobized methylated particles, DBTDL as catalyst, DR, modified with hydrophobized octylated particles, DBTDL as catalyst, DO, catalyzed by octylamine, DD, catalyzed by dodecylamine, DH, catalyzed by hexadecylamine.

2.2. Physico-chemical characterization of the gels obtained from modified ethylsilicate consolidants

The course of the hydrolysis and polymerization of ethylsilicate oligomer Dynasylan 40 in isopropanol catalyzed by dibutyltin dilaurate was followed by IR reflection spectroscopy (Nicolet 6700 FT-IR). For the IR measurements, a thin layer of ethylsilicate sol was deposited by dip-coating (Coater 5 AC, ID-Lab) on an aluminum foil fitted to a glass sheet.

The porosity of gels dried at 60 °C was determined by the analysis of adsorption isotherms of nitrogen at the boiling point of liquid nitrogen (ca 77 K). Before the adsorption experiment the samples were outgassed at 60 °C for 24 h to ensure the complete cleaning of the surface. The experiments were carried out using an ASAP2010 apparatus (Micromeritics). Because of the complex character of the samples' porosity the obtained isotherms were analyzed by a combination of several methods, especially the Broekhoff-de Boer t-plot and several variants of the NLDFT. The pore width is described using the IUPAC nomenclature, micropores, mesopores and macropores corresponding to the width of less than 2 nm, 2–50 nm and more than 50 nm, respectively.

2.3. Properties of sandstone substrates used

Consolidants were tested on two types of sandstone with similar mineralogical composition, namely Mšené and Hořice (locations of quarries in the Czech Republic), with different porosity and strength. Sandstone Hořice is significantly stronger (bending strength almost 3 times higher) than sandstone Mšené (Table 5) and less porous (Table 2). Sandstone Mšené with low bending strength was used as a material with characteristics similar to those of weathered sandstone. Hořice sandstone is an ocher colored fine-grained clastic sedimentary rock consisting mainly of quartz clasts (98%) and containing clay matrix (kaolinite, often impregnated with iron-oxyhydroxides). Mšené sandstone is a white-greyish fine-grained sedimentary psammitic rock [13] containing quartz as a major mineral (99%) and muscovite and feldspar clasts as accessories. The matrix is formed by clay minerals (kaolinite, chlorite) but its content is very low (<0.5%). Both stones have been widely used as building, architectural and sculptural materials in the Czech Republic. Texture properties of stones obtained by mercury porosimetry are given in Table 2.

2.4. Testing the mechanical properties of consolidated sandstones

2.4.1. Nanoindentation

The goal of nanoindentation testing is to obtain elastic modulus and hardness of the specimens. It can be carried out by contacting an indenter tip of known geometry with the sample surface. The samples were tested with Hysitron TI 750L Ubi nanoindentation instrument. A three-sided pyramidal diamond Berkovich indenter and the Oliver-Pharr method were used to get the elastic modulus and hardness. In a typical test, force and depth of penetration are recorded. Fig. 1 shows a typical load (P)-depth (h) curve, where P_{max} is the maximum load. Initial unloading stiffness S is defined as follows [14]:

$$S = \frac{dP}{dh} = \frac{2E^*\sqrt{A}}{\sqrt{\pi}} \Rightarrow E^* = \frac{1}{2}\frac{\sqrt{\pi}}{\sqrt{A}}\frac{dP}{dh} \quad (1)$$

$$\frac{1}{E^*} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu_i^2)}{E_i} \quad (2)$$

where A is the projected contact area at load values peak, E^* is the reduced elastic modulus and E and ν are Young's modulus and Poisson' ratio for the sample and E_i and ν_i are the same parameters for the indenter tip [15], respectively. For Berkovich indenter used in these experiments the elastic modulus E_i and Poisson' ratio ν_i are 1140 GPa and 0.07, respectively. Each gel sample was scanned by in-situ Scanning Probe Microscopy (SPM) imaging to select a suitable place for experimental testing with minimum roughness. Maximum load was P_{max} = 1.0 mN, being increased linearly for 5 s to reach maximum, which was held for 2 s and then full unloading was achieved within 5 s. Load curve is shown in Fig. 1.