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Design, synthesis and characterization of hybrid coatings suitable for geopolymeric-based supports for the restoration of cultural heritage

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Abstract. Geopolymers are inorganic materials that form long-range, covalently bonded, networks; they are materials similar to ceramics, whose components are mainly aluminium and silicates. Any inorganic source of silica and alumina, dissolved in the alkaline solution, acts as a precursor of geopolymers. The type of clays most commonly used in the synthesis of geopolymers is based on kaolinite. The present work concerns the modification of the geopolymer at the chemical and nanostructural level, through the design and development of hybrid coating sol-gel formulations to improve characteristics such as mechanical strength, chemical inertness, heat resistance and porosity for possible use in the restoration and conservation of cultural heritage. The methods of functionalization of the geopolymers here shown are: (i) the treatment of the geopolymeric surface, post-drying, through the application of the sol-gel directly on the monolith, for a modification of the surface properties; (ii) the pretreatment of the geopolymeric mixture, through the addition of the alkoxysilane which can induce a homogeneous consolidation of the molecular structure, implementing the properties of the entire monolith. The employed alkoxysilanes differ according to the length of the hydrocarbon chain and the presence of halogen atoms. Hydrophobicity tests were performed on these formulations.

1. Introduction

The term "geopolymer" describes a wide variety of natural or synthetic composite materials showing a polymeric structure [1-3]. They are materials similar to ceramics, whose components are mainly

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aluminium-natural silicates (see figure 1) [4-6], although this class of compounds can easily be extended to all inorganic polymers present in nature, such as phosphates (apatites), borates, vanadates and arsenates [7-13]. The geopolymerization takes place in three phases: dissolution of the aluminosilicate source, polycondensation of aluminosilicate oligomers and finally precipitation of geopolymeric particles, which form a gel. Geopolymers have many advantages over traditional organic polymers, deriving their main characteristics from the starting mineral components and improving their chemical-physical and mechanical properties [14-21]. The sol-gel synthesis is an eco-friendly approach to functionalize geopolymers, without high-temperature treatments, perfectly in accordance with the principles of circular economy and green chemistry [22-25]. The alkoxysilane agents may be chosen for the implementation of specific properties of the geopolymer materials that allow the production of various types of coatings, such as protective coating, reflective or anti-reflective coatings, refractory linings, coatings with controlled porosity; all these properties may result determining in the restoration of cultural heritage [26-27].

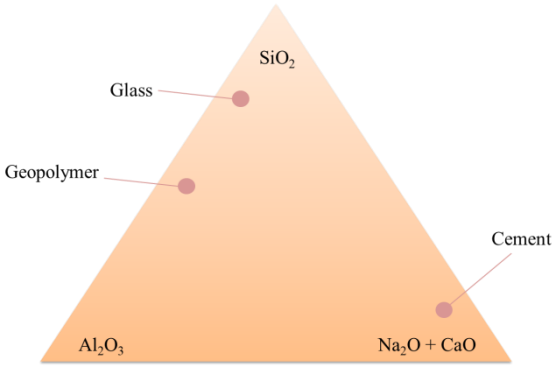

Figure 1. Geopolymer composition scheme.

2. Experimental section

2.1 Materials and Methods

Any inorganic source of silica and alumina, dissolved in the alkaline solution, acts as a precursor of geopolymers and therefore lends itself to geopolymerization [20-21].

Raw materials used in the geopolymerization process are: Kaolin, Diatomite, Montmorillonite, Volcanic Ash and Blast furnace slag. Each of the materials listed above is alkaline activated, using as alkaline activators NaOH 7M (28% w/w), 9M (36% w/w), and KOH 7M (39.2% w/w), 9M (50,4% w/w) and geopolymerized, keeping the temperature below 100°C. NaOH, KOH, *Tetraethyl orthosilicate* (TEOS, Figure 2), *(3-Aminopropyl) triethoxysilane* (APTES), (3,3,3-trifluoro-propyl) trimethoxy silane (F3) and *1H,1H-2H,2H-perfluorooctyl triethoxy silane* (F13) were purchased at the highest purity level and used as received by STREM Chemicals, inc. without any further purification.

X-ray diffraction analysis (XRDP) was performed by a BRUKER D8 ADVANCE diffractometer with radiation Kα of Cu with Bragg-Brentano theta-theta geometry, equipped with a SiLi detector at solid state "Sol-X". The acquisition conditions are 40 kV and 40 mA. The diffractograms were obtained with scans from 2 to 70/80 degrees 2θ, with stepsize of 0.02 degrees 2θ, with a count time of 1 second. The diffractograms were filtered by Kα2 (Fourier filter). The positions of the peaks were compared with those of the database ICDD JCPDS.

Geopolymerization process is schematized in Figure 3 and consists of three steps:

1. Dissolution in alkaline solution, to induce the exfoliation of the tetrahedral layers of aluminates and silicates;
2. Condensation in aqueous solution with formation of a gel phase;
3. Solidification of the gel in a modified 3D structure with the intercalation of water and Na^+ and K^+ cations between the aluminosilicates layers.

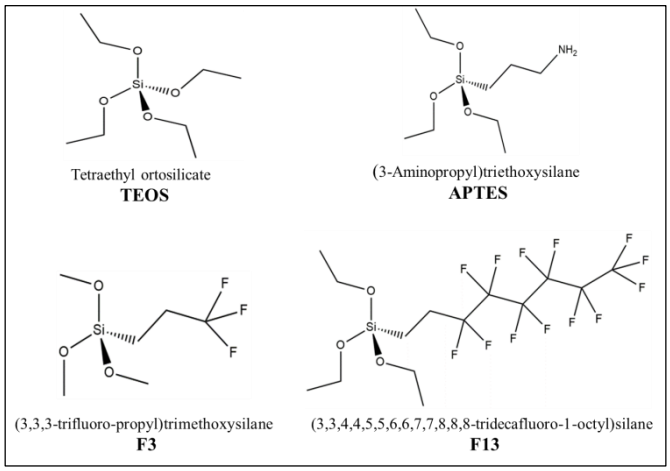

Figure 2. Sol-gel alkoxysilane precursors.

A typical procedure [28] to prepare the sol-gel solutions is as follows: TEOS (2.013g) and APTES (0.943g), together with an equimolar amount of an organic silane (F3 or F13), was dissolved in 25 mL ethanol. The resulting mixture was vigorously stirred at room temperature for 12 hours, and then ultrasonicated for 30 min to get a homogeneous suspension, and then used as coating or in addition to the geopolymeric mixture.

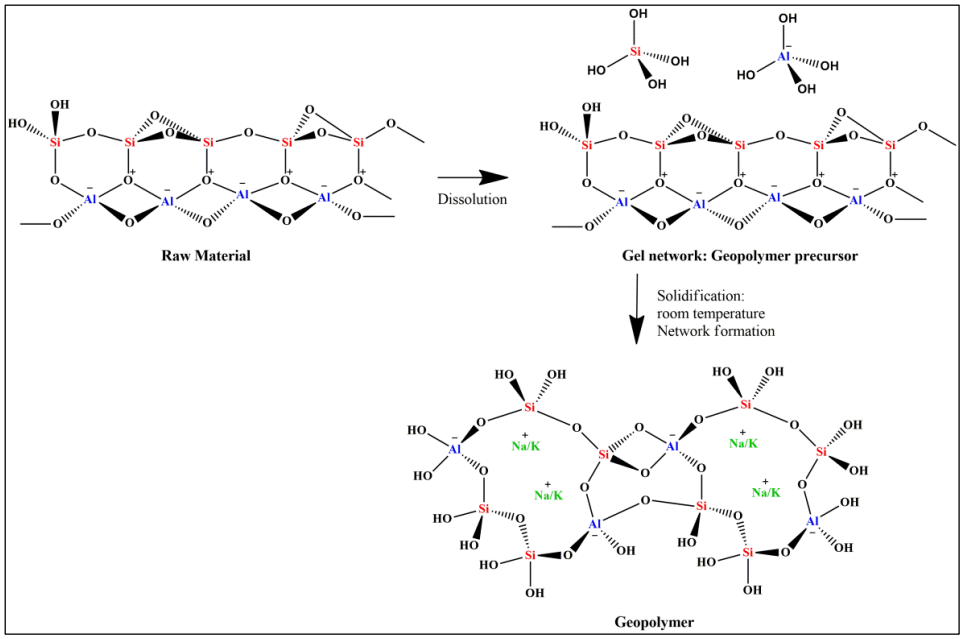

Figure 3. The chemistry of geopolymerization process.

3. Results and discussion

3.1 Sol-gel synthesis and geopolymer functionalization

As shown before [29-35] for similar functional silica based coatings, the employed sol–gel mixtures were made from *Tetraethyl orthosilicate* (TEOS) and *(3-Aminopropyl) triethoxysilane* (APTES) precursors undergoing hydrolysis–condensation reactions in several steps in combination with two alkoxysilanes, namely (3,3,3-trifluoro-propyl) trimethoxy silane (F3) and *1H,1H-2H,2H-perfluorooctyl triethoxy silane* (F13), employed individually. Associated condensation reactions are

directly related with the removal of water from the polymer matrix resulting in the formation of more stable silica 3D-networks, through drying and curing processes performed at room temperature for 24h or at T=100°C for 30' following by further 30' at T=140°C.

The most important benefit of using sol-gel method concern the formation of alkoxysilane layer or xerogel at room temperature. Since there are no decomposition products formed, one can produce thick films or composite with little stress and low energy consumption. A conventional synthesis for the functionalization of geopolymers (Montmorillonite is used as aluminosilicates source) can be performed by following two different synthetic approaches, as following: (i) the treatment of the geopolymeric surface, post-drying, through the deposition of the sol-gel directly on the monolith, producing a thin film for a modification of surface properties; (ii) the pretreatment of the geopolymeric mixture through the addition of the alkoxysilane sol-gel coatings which can induce a homogeneous consolidation of the molecular structure, implementing the properties of the entire monolith. The morphology of the geopolymer surface depends on the degree of cross-linking of its molecular structure and varies according to the quantity and type of alkoxysilane added. A green method to implement these properties consists of incorporation of coupling silane agents and organic fillers during the geopolymerization process. Additionally, the surface treatment is carried out using the above discussed alkoxysilanes mixtures, which differ according to the length of the hydrocarbon chain.

3.2 Characterization

The preliminary characterization of the clays was carried out by means of powder X-ray diffraction analysis (XRDP), thus identifying the type of clay and its chemical composition (figure 4). The peaks resulting from the diffraction spectrum on powders for clay minerals can be distinguished by intense diffraction peaks, such as: quartz, feldspars, zeolites, carbonates. Mixed-layered clays are formed with two or more types of clays that alternate in overlapping layers and are more difficult to interpret by XRDP analysis, so more analyses are generally required.

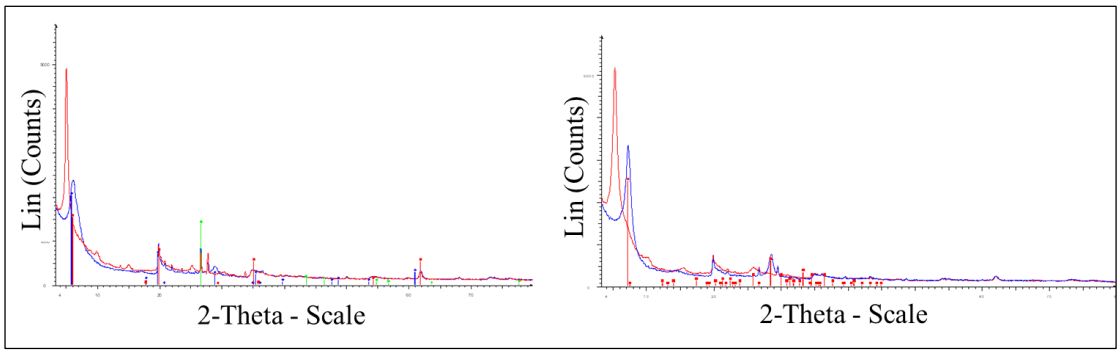

Figure 4. Powder X-ray diffraction spectra (XRDP) for two types of clays (Montmorillonite) before (blue line) and after (red line) functionalization, with TEOS_APTES/F3 formulation on left side and TEOS_APTES/F13 formulation on right side, respectively.

In both diffractograms, the first peak detected suffered a left shift in the functionalized clay, thus indicating a probable removal of the layers characterizing the mother clay and therefore an internal functionalization of the same.

3.3 Wettability tests

In the structured polymer, the alkoxysilane acts as a network inductor or as a network modifier inducing new properties to the matrix. The structural differences reflect the thermal hydrophobic properties of material determined by the addition of perfluorinated or long chain alkoxysilane species. These formulations can improve characteristics such as mechanical strength, chemical inertness, heat

resistance and porosity for possible use in the restoration and conservation of cultural heritage, as well as antimicrobial activities, low adhesive properties and no biocidal effects towards bacteria. In particular, the obtained materials have a surface that shows a hydrophobic nature (see figure 5 for preliminary hydrophobicity tests). Further studies on mechanical and antibacterial properties are actually in progress.

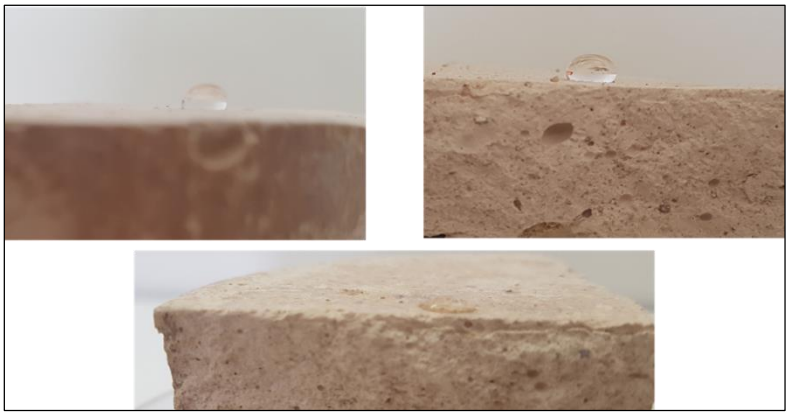

Figure 5. Hydrophobicity tests on Montmorillonite monolith treated with the sol-gel formulations. In the image above left, surface geopolymer is treated with TEOS_APTES/F3 formulation; in the image above right, surface geopolymer is treated with TEOS_APTES/F13 formulation; in the image below, the surface is treated with TEOS only.

4. Conclusions

The aim of this work was to synthesize a new functional geopolymeric matrix based on raw materials (like montmorillonite or other clays, volcanic ashes or Pozzolan, and waste materials like fly ashes or blast furnace slags), and hybrid sol-gel to modify its properties. The employed sol-gel synthesis utilizes an eco-friendly approach to prepare and functionalize geopolymers, without high-temperature treatments. These kinds of formulations are widely used for their hydrophobic, anti-abrasive, antibacterial and antifouling action. In particular, in the first phase of this work, we tested a simple procedure for the production of a polymeric hybrid sol-gel, which was applied to the geopolymers both in the pre-treatment phase and after drying. The effectiveness of the previously mentioned properties is evaluated by wettability tests, while further studies are in progress.

Acknowledgments

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