



Structure and micro-nanomechanical characterization of synthetic calcium–silicate–hydrate with Poly(Vinyl Alcohol)



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ABSTRACT

The principal phase of hardened Portland cement pastes is calcium silicate hydrate (C–S–H), which influences the physical and mechanical properties of construction materials. In this work calcium silicate hydrate (C–S–H) was synthesized, with the addition of Poly(Vinyl Alcohol) (PVA), for the development of C–S–H/polymer nanocomposites. Among the polymers available, PVA is indicated by the literature as one of the most viable for producing C–S–H/polymer complexes. However, no consensus exists regarding the kind of interaction. The resulting compounds were characterized by XRD, FT-IR, TGA, carbon content (CHN), TEM, SEM and elastic modulus and hardness were measured by instrumented indentation. The set of results presented do not confirm the intercalation of PVA in the interlayer space of C–S–H, but presented evidence of the potential for intercalation, since changes in the structure clearly occurred. A significant change in the micro-nanomechanical properties of C–S–H occurred in the presence of PVA.

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1. Introduction

It is well known that calcium silicate hydrate (C–S–H), the main product from Portland cement hydration, has a significant influence on most physical and mechanical properties of cement-based materials. C–S–H is considered a lamellar, crystalline semi-continuum and inherently complex material, particularly in relation to its “bond” nature forces (iono-covalent forces between individual C–S–H layers or C–S–H layer stacks, separated by strongly localized calcium ions and water molecules), consisting of order-disorder lamellae stacking of particles, where each lamellae is formed by stacking sheets (approximately 12 under the best synthesis conditions) and each sheet has a central Ca–O sheet that has silicate chains on both sides, which are kinked with a periodicity of three tetrahedra; these chains are called dreierketten [1]. C–S–H is similar to the tobermorite–jennite like nanostructure crystal [2], with a complex structure; it is intrinsically fragile with a low flexural strength [1,3]. The complex nanostructure of C–S–H makes it an excellent candidate for the manipulation and control of its properties, through the intercalation of organic molecules, for the fabrication of C–S–H/polymer nanocomposites [4]. The advancement of nanoscience through the development of C–S–H/nanocomposites

is important for the production of materials that are more efficient in relation to the binding forces [5,6], thus improving the tensile strength and avoiding the cracking problems inherent to concrete and mortar, which are widely used by the construction industry. Nature has shown that the mixture of organic and inorganic materials is a potential route for the elaboration of more efficient materials; teeth and bones are good examples.

The development of C–S–H/polymer nanocomposites was initiated in 1999 by Matsuyama and Young [7–11], who verified that among the polymers evaluated, anionic (poly-acrylic acid – PAA and poly-metacrylic acid – PMA) and cationic polymers (poly-diallyldimethylammonium chloride – PDC) intercalated in the C–S–H structure, presenting expansions in the nanostructure between 1.04 nm and 0.91 nm, respectively, while absorption of the neutral polymer, PVA (78,000 g/mol), alters the interlayer spacing nonsignificantly (<0.20 Nm) [9,11], causing an increase in the interlayer spacing of 0.10 nm.

Later Mojumdar and Raki [12] tried to merge the PVA polymer with the nanostructure of C–S–H and observed an increase in interlayer spacing of 0.14 nm, along with changes in the connections between the silica tetrahedra – dreierketten (using the FT-IR technique) – concluding that intercalation and the formation of a C–S–H/PVA nanocomposite occurred. While studying ceramic tile systems, Mansur and Mansur [13] verified the overall result of adherence between porcelain tiles and polymer modified mortars could be explained by the nano-order structure, through the increased adhesion between tile and mortar, due to the formation

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of a hybrid ceramic–polymer–ceramic interface by hydrogen bonds between PVA hydroxyl groups and silanol from the tile surface and water from the nanostructured C–S–H gel interlayer.

On the other hand, Merlin et al. [4] observed no changes in the interlayer spacing in the C–S–H/PVA synthesis (molecular weight of 78,000 g/mol), nor when using other polymers similar to those tested by Matsuyama and Young [7–11], suggesting that the polymer is absorbed between the C–S–H particles. The overall results of the literature indicate that the success of intercalation depends on the molar ratio of the Ca/Si of C–S–H, the nature of the polymer (whether it is cationic, anionic and nonionic) and its molecular weight, and the synthesis process. A recent study [14] has provided evidence for the adsorption and intercalation of polyethylene glycol (PEG) polymers on the surface and into the interlayer spaces of the C–S–H structure (alter the interlayer spacing from 1.5 nm to 4.5 nm). It has also been reported that the presence of PDC in 0.8Ca/Si C–S–H affects both its nano and mesostructure: (i) the broadening and slight shift in the 002 basal reflections (XRD) and the alteration in C–S–H Si–O–Si bonding (FT-IR) indicate that a part of the PDC is intercalated between the C–S–H lamellae, and; (ii) the remaining PDC is probably adsorbed on the surface or in the void space left by the C–S–H particles, affecting its packing density, consequently, significant alterations in the mechanical properties of C–S–H in the presence of PDC were verified [15].

Although numerous studies have observed changes in nanostructures and have associated these changes with the mechanical behavior of the materials, mechanical tests using instrumented indentation in C–S–H/PVA complexes have never been performed. Thus, this study evaluated the chemical and micro-nanomechanical properties of C–S–H synthesis modified with the PVA polymer, aiming to contribute to the development of C–S–H/polymer nanocomposites.

2. Materials and methods

C–S–H and C–S–H/PVA were produced by the direct precipitation method [9,11]. PVA polymer solution was used at 98% hydrolyzed (13,000–23,000 g/mol – [–CH₂CHOH–]_n). A 1 mol/L calcium nitrate solution was added gradually to a 0.22 mol/L solution of sodium silicate with the polymer (except for pure C–S–H) pre-dissolved in CO₂-free deionized water to achieve a 0.8 Ca/Si ratio. Chemical analysis by XRF (Table 1) showed that the final Ca/Si ratio (0.60 for C–S–H and 0.57 for C–S–H/PVA) remained proportional to the initial project value. The PVA concentration was 0.5 g/g Ca salt [11]. The total water:solid ratio was 20:1. The pH of the mix was maintained between 13.1 and 13.3 with a NaOH solution (10 mol/L). After maintaining the suspension at 60 °C for 35 days under gentle stirring in a CO₂-free atmosphere, the precipitates were vacuum-filtered and washed with acetone and CO₂-free deionized water to eliminate the residual polymers and sodium nitrate ions. Next, the precipitates were dried at 60 °C in a vacuum oven for 14 days. One part of the precipitate was ground in an agate mortar and sieved (# 75 μm) for XRD, FT-IR, TGA and carbon content (CHN), while the other part (small irregular particles) was vacuum-impregnated in 2 cm × 2 cm cylinders with a low viscosity resin and cut with a diamond saw for nanoindentation tests. For TEM observations (JEOL, 100 kV), the ground precipitates (before drying) were dispersed in ethanol and dripped onto a

400-mesh copper grid covered by a carbon film, after which the grid was placed in a vacuum desiccator for 24 h.

The cylinder surface was then ground with silicon carbide papers and polished with diamond pastes (four stages of increasing fineness) to obtain a very flat, smooth surface finish. After each grinding/polishing stage, the samples were placed in an ultrasonic bath to remove the dust and diamond particles left on the surface or in the porous structure.

Nanoindentation was performed using a nanoindenter XP (MTS System). The unpolished surface of the cylindrical specimens was carefully cut with the diamond saw into sections that were 5–6 mm thick. Twelve indentations were performed in each sample in three different regions (for each region, four individual indentations were performed in 2 × 2 matrices, with 20 μm spacing) by applying five loading cycles of 2, 4, 8, 16, and 32 mN in each indented location (matrix 1). An additional test was performed using higher loads (matrix 2), in order to evaluate both the nano- and microstructure of the material over a larger area, verify the homogeneity of the material and make marks that would be visible under SEM, thus achieving a more in-depth interpretation of the results by combining the characteristics of the microstructure, morphology and fractures, with the nanomechanical properties. In this case, a 2 × 3 points matrix was used up to a load of 512 mN (1, 2, 4, 8, 16, 32, 64, 128, 256, and 512 mN). Loading was applied linearly for 10 s. The maximal load (P_{max}) was then maintained for 5 s, and unloading occurred over an additional 10 s. Hardness (H) is defined as the mean pressure that a material can support under load, and is determined by [16,17]:

$$H = \frac{P_{max}}{A(h_c)} \quad (1)$$

where P_{max} is the maximum applied load and $A(h_c)$ is the projected contact area function which corrects for the Berkovich tip rounding effect.

The elastic modulus of the material is determined by [18]:

$$E = \frac{1 - \nu^2}{\left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}\right)} \quad (2)$$

where E_r is the reduced elastic modulus, E_i and ν_i are the indenter elastic modulus and Poisson ratio, and E and ν are the elastic modulus and Poisson ratio of the material respectively. For diamond, $E_i = 1141$ GPa and $\nu_i = 0.07$ [16,17]. Based on relationships developed by Sneddon [19], an expression was derived for the reduced elastic modulus, E_r [16,17]:

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A(h_c)}} \quad (3)$$

where $S = (dP/dh)$ is the stiffness obtained experimentally from the upper part of the unloading curve and β is a constant dependent on the indenter geometry, being equal to 1.034 for a triangular symmetry [16–18]. After nanoindenter testing, the sample was removed, coated with a gold layer and examined by SEM. The chemical analysis of the main elements was performed by EDAX.

XRD was performed to detect shifts in the C–S–H 002 basal reflections, which are due to polymer intercalation. A Philips X'pert instrument was used that operates with Cu K α radiation ($\lambda = 1.5418$ Å) with an output of 40 kV and 30 mA. Scanning was performed from 2° to 10° (2 θ) in 0.02° steps, with a collection time of 5 s per step. A Perkin–Elmer 16PC Fourier transform-infrared spectrometer (FT-IR) was used in direct transmission mode ranging from 4000 to 400 cm⁻¹ (4 cm⁻¹ resolution), and the carbon content was determined by CHN (carbon, hydrogen, nitrogen – EA 1100 CE Instruments) elemental analysis. The thermogravimetric analysis (TGA) was performed on samples of approximately

Table 1
Chemical analyses of the C–S–H and C–S–H/PVA (XRF).

Oxide (mass %)	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	LOI
C–S–H	56.80	31.23	0.18	<0.05	–
C–S–H/PVA	56.61	30.47	<0.05	<0.05	–

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