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Modification of poly(ethylene glycol) on the microstructure and mechanical properties of calcium silicate hydrates

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ABSTRACT

With the aim of creating more sustainable building materials, calcium silicate hydrate (C-S-H), the primary binding phase in modern concrete, was integrated with poly(ethylene glycol) (PEG). At the crystal lattice scale, synchrotron radiation-based high-pressure X-ray diffraction (HP-XRD) reveals that the incorporation of PEG increases the ab-planar stiffness of C-S-H leading to a higher bulk modulus, while molecular simulation results indicate polymers are not likely intercalated into the interlayer region. At a higher length scale, nanoindentation measurements show the introduction of PEG lowers the packing density of C-S-H particles and, thus, decreases the indentation modulus. However, a high creep resistance of the C-S-H/PEG sample is still maintained, which suggests a meso-composite may form to restrict the rapid translation between neighboring calcium silicate sheets. Furthermore, ^{29}Si nuclear magnetic resonance (NMR) shows that the presence of PEG shortens the mean chain length of C-S-H, making dimer the predominant structure.

1. Introduction

As the primary hydration product of Portland cement (PC), calcium silicate hydrate (C-S-H) can be considered as the key component of PC concrete. The microstructure of C-S-H determines the cohesion mechanisms between solids, and the transport of water and aggressive ions through hierarchical pores, which are critical to the mechanical and durability properties of concrete at the macroscale [1–5]. Therefore, to create more sustainable construction materials and lower the carbon footprint, structural modification and performance optimization of C-S-H are urgently demanded. One approach includes the fabrication of organic/inorganic composites. Given the significant role of polymers on improving the performance of clay-based systems [6–8] that possess similar lamellar structures to that of C-S-H, it is believed that polymers can also enhance C-S-H in a comparable way.

Indeed, previous investigations have proved the positive effects of polymer modifications on the C-S-H matrix [9–16]. Matsuyama et al. developed original research on C-S-H/polymer composites and proposed a series of polymers that could be intercalated into the interlayer region, affecting the stacking of C-S-H [17–19]. In addition to intercalation, flocculation and exfoliation in nanocomposites are also possible interaction mechanisms with the introduction of polymers to C-S-H [20], and recent molecular dynamics simulations have unraveled the interfacial connection mechanisms between the distinct polymer functional groups and the calcium silicate phases [21,22]. With organic modifications, the elastic modulus of the substrate was increased by 40–100% in the presence of a novel copolymer (poly-dimethylacrylamide and poly(butadiene-goxyethylene) silylated with T-silanes) [10], while the storage modulus was also increase by the introduction of another polymer species (polyaniline) [13]. In terms of durability, Rouhollah et al. showed that polyaniline was able to limit the transport of aggressive ions and improve the volumetric stability of C-S-H when it was subjected to salt solutions [11,13]. Among the diverse polymer types, poly(ethylene glycol) (PEG) is one of the most promising candidates for C-S-H modification. At the macroscale, the addition of PEG could increase the fracture energy of ordinary Portland

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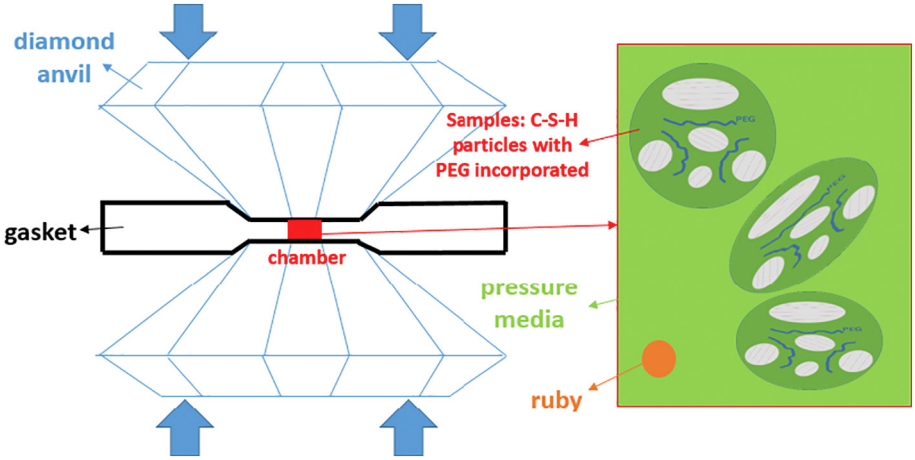

Fig. 1. An axial Merrell-Bassett cell assembly used for HP-XRD measurements.

cement paste [23]. At the microscale, the layer and pore structure of C-S-H were greatly modified by PEG, as detected by scanning transmission X-ray microscopy [24] and Fourier transmission infrared spectroscopy [25], respectively. The possible intercalation of PEG into the interlayer of C-S-H was also concluded by comprehensive analysis of the results of X-ray diffraction (XRD), thermogravimetric analysis (TGA), and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) [12]. Furthermore, Zhou et al. demonstrated that, when subjected to tensile loading, the intercalated PEG could be filled into the defects of the silicate chains, thereby increasing the system connectivity and improving the ductility of C-S-H, which was consistent with the experimental results at the macroscale [16].

However, direct experimental data of the structure-mechanical property relations of C-S-H/PEG composite at the lattice scale is still missing due to the limitations of laboratory-based equipment. Regular techniques (e.g., nanoindentation) measure the indentation modulus and hardness of samples at the scale of several μm [26,27]. This resolution fails to reflect the real mechanical properties of pore-free C-S-H solids because pores with the width lower than several μm, which are commonly present in the C-S-H samples [2], strongly affect the measurement results. High-pressure XRD (HP-XRD) based on the synchrotron radiation allows probing of the nanoscale volumetric strain of C-S-H solids induced by compressive loading, and thus, the bulk modulus can be obtained directly. With this technique, the effect of the nanopores is completely eliminated since the uniform pressure can be generated everywhere inside the C-S-H samples by the all-pervading and in-depth penetration of a liquid pressure medium [28,29]. HP-XRD has been employed to successfully measure the bulk modulus of cement-based phases (e.g., tobermorite [30], tricalcium aluminate [31], calcium aluminate hydrate [32], tetracalcium aluminum carbonate [33]), and the results agree well with the ab initio calculations [34,35]. Recently, by taking advantage of HP-XRD, Geng et al. obtained the bulk modulus of C-(A-)S-H samples with different calcium to silicon (Ca/Si) and aluminum to silicon ratios (Al/Si), and they elucidated the densification of interlayer spacing and the dreierketten chain cross-links, both of which strengthened the atomistic scale mechanical properties of C-(A-)S-H [28,29].

In this work, HP-XRD is employed to elucidate the influence of PEG incorporation on the structure and mechanical properties of C-S-H at the molecular scale. ^{29}Si MAS NMR and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) are performed to understand the effects of PEG modification on the local chemical environment and composition of C-S-H, while nanoindentation measurements illustrate the interactions between the organic and inorganic phases at the mesoscale.

2. Materials and methods

2.1. Synthesis of C-S-H and C-S-H/PEG samples

C-S-H sample with a calcium to silicon ratio (C/S) of 1.3 was synthesized by mixing stoichiometric amounts of calcium oxide (CaO), fumed silica (SiO_2), and deionized water. The C/S of 1.3 was commonly used in C-S-H/polymer studies [17–19] and was able to guarantee the absence of the distinguishable portlandite phase [36]. The calcination of pure calcium carbonate at 900 °C for 24 h was carried out to produce highly reactive CaO, and fumed silica was from Cabosil-5000. Deionized water was boiled to remove dissolved carbon oxide (CO_2) before mixing with CaO and SiO_2 at a solid-to-liquid ratio of 1:40 in polypropylene containers. Once the reactants were mixed, nitrogen gas was fluxed into the container to prevent carbonation. Continuous gentle agitation was applied to the samples for two months to ensure a homogenized reaction. Afterwards, the synthesized C-S-H was centrifuged and washed twice in a glove box filled with nitrogen gas and then transferred to a vacuum oven for 72 h of drying. Finally, samples were stored in a vacuum desiccator until measurements. The C-S-H/PEG sample was synthesized using a method similar to that described above but with the addition of PEG to CaO and SiO_2 during the mixing process. The amount of PEG was a 3% mass proportion of the solids (CaO + SiO_2), and the average molecular weight was 2000.

2.2. High-pressure XRD

The HP-XRD measurements were obtained at beamline 12.2.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL) [37]. As shown in Fig. 1, an axial Merrell-Bassett cell assembly, which was composed of a stainless-steel gasket and diamond anvils with culet diameter of approximately 400 μm, was employed to conduct the high-pressure XRD experiments. Each gasket had a cylindrical chamber in the center to place samples. To generate a chamber hole of 150 μm-diameter and 100 μm-height, the central region of the gasket was first indented by a diamond anvil and then drilled by a laser. Afterwards, samples were placed into the chamber along with a small amount of ruby powder (α-Al_2O_3 doped with 0.05 wt% Cr^{3+}), which acted as an indicator of internal pressure by fluorescence signal [38]. The chamber was closed by diamond culets, which were filled with an ethanol-methanol solution (the ratio was 1:4 by volume). This solution was able to penetrate into the pores with diameters as small as 1 nm [39], ensuring that samples were subjected to hydrostatic pressure at the nanoscale. The hydrostatic pressure was generated by applying a load on the diamond anvils along the direction parallel to the incident beam path. Several pressure values lower than 10 GPa were generated almost