Intercalation of Polymers in Calcium Silicate Hydrate: A New Synthetic Approach to Biocomposites?

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In recent years there has been considerable interest in the formation of ceramic−polymer composites using a variety of synthetic routes.[1−3] However, in most cases nonaqueous approaches have been used. Biocomposites (bone, tooth, shell, etc.) are developed through the development of ordered structures of mineral phases from aqueous media templated by protein polymers. However, such composites are limited to biopolymers combined with a restricted number of mineral phases (apatite, calcite, aragonite) as the inorganic components. The aqueous synthesis of analagous inorganic/organic composites using synthetic polymers and a wider range of inorganic phases would spur the quest to emulate these natural composites in the laboratory.

Although the intercalation of small organic molecules is well-established in clay minerals,[4] and related layer structures such as calcium aluminate hydrates,[5,6] instances of polymer intercalation are rarer. Steric and entropic factors might be expected to hinder the easy entry of macromolecules into preformed layer structures. Some synthetic polymers can intercalate with clay minerals,[7] although many others can only adsorb on external surfaces. Intercalation of poly(vinyl alcohol) (PVA) into the layer structure of $4CaO \cdot Al_2O_3 \cdot 11H_2O$ can occur during its crystallization,[8] but not after the structure has formed. This hydrate has a structure similar to that of clays, but with a positive layer change balanced by interlayer anions.[9] Poly(ethylene oxide) has been intercalated from aqueous solution into the layer structure of colloidal $V_2O_5 \cdot xH_2O$.[1,10]

Here we report the first intercalation of polymers into the structure of calcium silicate hydrate (C−S−H) during its precipitation from supersaturated solution and show how structural variations influence complex formation. C−S−H is the major product of Portland cement hydration, where it forms as an amorphous phase of variable composition. C−S−H is thought to

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(10) Liu Y.-J.; DeGroot, D. G.; Schindler, J. L.; Kannewarf, C. R.; Kanatzidas, M. G. *Chem. Mater.* **1991**, *3*, 992.
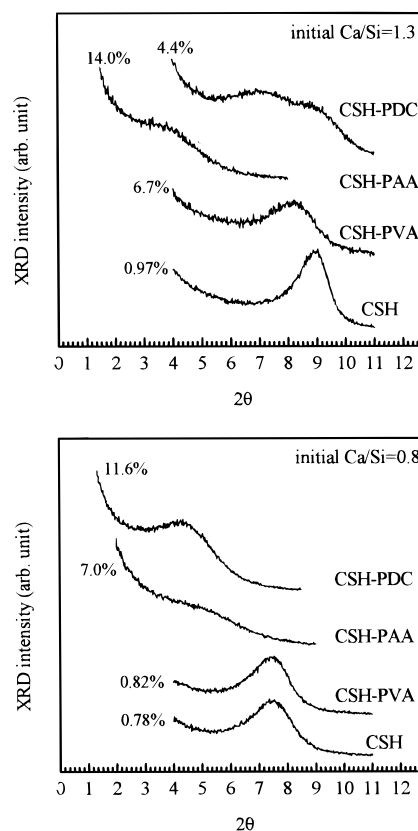

Figure 1. Changes in (002) basal spacing of C−S−H precipitated with different polymers. Percentages are weight percent of carbon in the complexes.

form a layer structure related to tobermorite and jennite.[11] We show that variations in C−S−H composition lead to variations in the intercalation abilities of different polymers, implying that the inorganic structure may play a templating role. These preliminary results suggest that hydrate chemistry may offer a general route to the formation of synthetic analogues of biocomposites.

C−S−H/polymer complexes were prepared by gradually adding calcium nitrate solution (1 mol/L) with continual stirring to sodium silicate ($Na_2O \cdot SiO_2 \cdot 9H_2O$) solution, which was predissolved with polymer in deionized water. (Polymer concentrations were 6.2 g/L^{-1} (PVA), 10.2 g/L^{-1} (PAA), and 42.5 g/L^{-1} (PDC) for optimum formation of the complexes.) The initial Ca/Si molar ratio is controlled by varying the amount of sodium silicate added. Three polymers, nonionic poly-(vinyl alcohol) [PVA, 99.7 mol % hydrolyzed, MW = 78 000 Da], anionic poly(acrylic acid) [PAA, MW = 90 000 Da], and cationic poly(diallyldimethylammonium chloride) [PDC, MW = 100 000−200 000 Da], were used in this study. The pH value was kept between 13.1 and 13.3 by adding NaOH during the precipitation of C−S−H. After aging at 60 °C for 7 days, the precipitates were separated and washed with deionized water to remove sodium and nitrate ions and any uncomplexed polymer.

(11) Taylor, H. F. W. *Cement Chemistry*, 2nd ed; Thomas Telford: London, 1997; pp 128−133.

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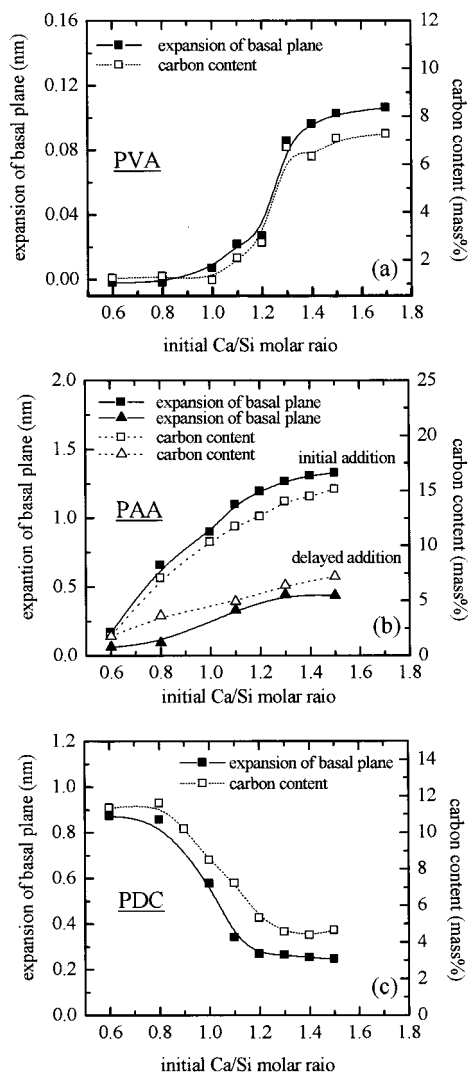Chem. Mater., Vol. 11, No. 1, 1999   17

Figure 2. Expansion of the basal spacing and carbon content of the C−S−H polymer complexes as a function of composition. (a) poly(vinyl alcohol); (b) poly(acrylic acid); (c) poly(diallydi-methylammonium chloride).

The precipitates were then washed with acetone and dried at 60 °C in a vacuum oven for 10 days.

Powder XRD patterns of the C−S−H/polymer complexes (Figure 1) show that when Ca/Si = 1.3 all three polymers can be intercalated, as indicated by the shift of the 002 basal reflections to smaller diffraction angles (indicating a larger interlayer spacing). Even the small shift associated with PVA is attributed to complex formation, since it cannot be accounted for by a change in the Ca/Si molar ratio of the complex. The full XRD pattern (not shown) has only six peaks up to 60° 2θ, with pronounced broadening indicative of considerable disorder in the structure. Unlike the 002 reflection, these peaks do not shift or broaden on the addition of polymer, being assigned to atomic distances within the layers. The degree of intercalation depends on the Ca/Si molar ratio of the initial solution and also increases as the polymer concentration increases, reaching a constant value when the ratio of moles of calcium in the starting solution to moles of polymer (expressed as monomer) = 1.0 (or 1.5 for the cationic polymer). Data covering the full range of starting Ca/Si molar ratios are shown in Figure 2. Changes in the interlayer spacing correlate well with the carbon content (meas-
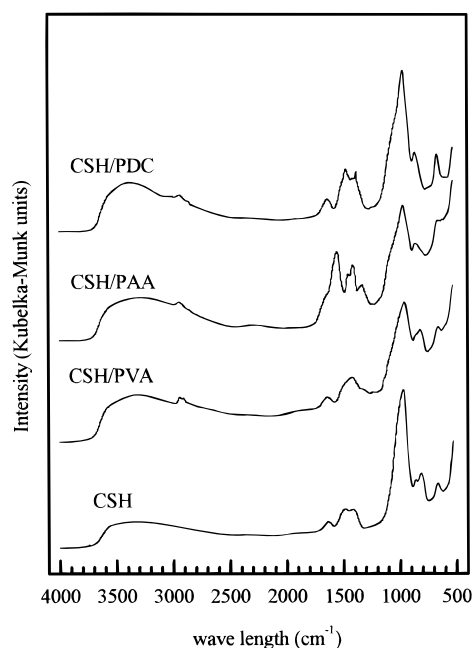

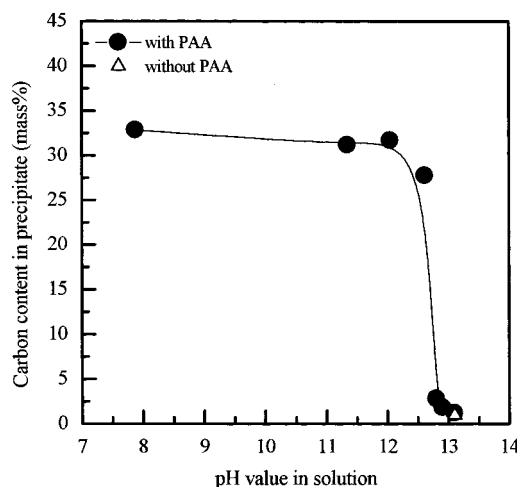**Figure 3.** Diffuse reflectance FT infrared spectra (DRIFTS) of C−S−H/polymer complexes.

Figure 4. Carbon content of solids precipitated from aqueous solutions of $Ca(NO_3)_2$ and poly(acrylic acid) as a function of pH. (Theoretical carbon content for calcium polyacrylate is 32.4%).

ured analytically by standard carbon, hydrogen, nitrogen analyses) and qualitatively with polymer-related features in infrared spectra.

DRIFTS spectra are presented in Figure 3. All spectra show CH_2 and CH stretching frequencies at 2936 and 2906 cm^{-1}. The PVA complex shows a broad band at 3300 cm^{-1} associated with the OH stretch in highly hydrogen-bonded PVA. The PAA complex has a doublet at 1550 and 1400 cm^{-1} attributable to an ionized carboxylate group, while the double bands at 1475 and 1383 cm^{-1} in PDC indicate that N^+-Cl^- has been replaced by the N^+-OH^- ionic bond. The possibility that the spectra merely indicate coprecipitation of the polymer with C−S−H was checked by adding only calcium nitrate to a solution of PAA and adjusting the pH. The calcium salt of the polymer precipitates until pH >12.5, when $Ca(OH)_2$ precipitates preferentially (Figure 4).

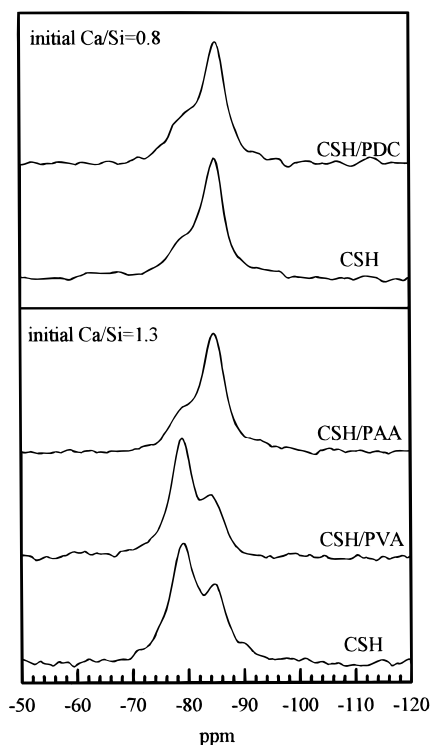^{29}Si solid-state NMR spectra are also presented in Figure 5. The doublet at −76 and −84 ppm correspond-

Figure 5. ^{29}Si NMR spectra of C−S−H/polymer complexes.

ing to Q^1 and Q^2 sites in the silicate chains, characteristics of C−S−H, are observed in all cases. The addition of PAA increases the Q^2 intensity, indicating lengthening of the chains, but this is not due to a change in the Ca/Si molar ratio of the precipitate.

Calcium and silicon analyses of precipitated solids show that the Ca/Si molar ratios lie close to the initial values at precipitation. Note that the cationic polymer PDC showed strong complex formation at low Ca/Si ratios but not at high values (Figure 2c), in contrast to the other polymers. While PVA cannot be intercalated if it is added after precipitation and aging of C−S−H, the PAA molecule will enter preformed C−S−H to a limited extent, as seen in Figure 2b, and PDC can be fully intercalated. In the case of PAA, a mixture of intercalated and normal C−S−H was observed, but the intercalated interlayer spacing was much lower.

Thermal analyses using combined TG−DSC show that the endothermic thermal decomposition of PAA in the C−S−H complex shifts to higher temperatures compared with a physical mixture of PAA and C−S−H. Residual carbon is retained after heating in the complex, but not in the mixture.

The complexing characteristics described above can be correlated with the variable structure of the C−S−H. C−S−H is amorphous when initially precipitated, but gradually transforms to a poorly crystalline structure, which is believed to be a defective tobermorite structure.[12] The crystal structure of tobermorite[13,14] is shown schematically in Figure 6.[14] The layers have infinite chains of silicate dreierketten condensed on both sides of a central Ca−O sheet. Ca^{2+} is located in the interlayer regions for charge balance along with water

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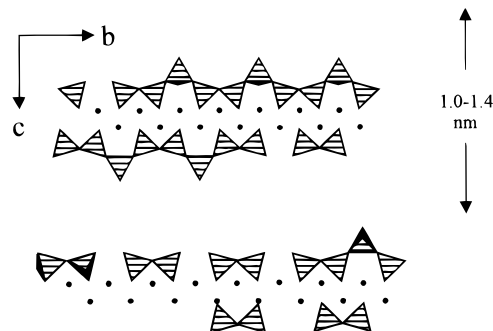(14) Taylor, H. F. W. *Zeit. Kristall.* **1992**, *202*, 41.

Figure 6. Schematic of the defective tobermorite structure showing layers composed of silicate dreierketten with missing tetrahedra and Ca atoms (filled circles): upper, Ca/Si < 1.0; lower, Ca/Si > 1.3. (After ref 12).
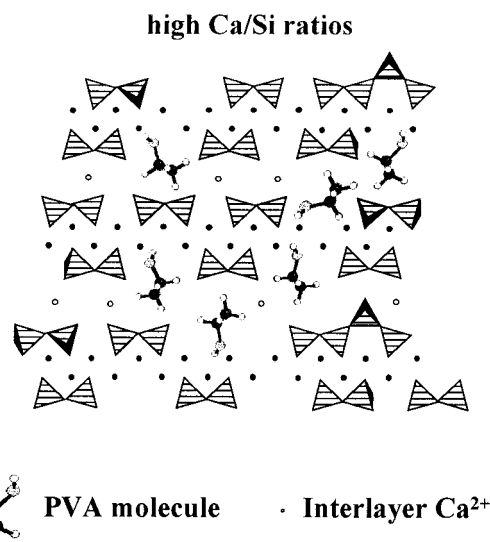

Figure 7. Schematic view (not to scale) of the proposed structure for the C−S−H/PVA complexes showing how the PVA molecule might fit into space created by the defective silicate dreierketten.

molecules. The ideal structure $[Ca_5Si_6O_{15}(OH)_2 \cdot xH_2O]$ has negatively charged layers and Ca/Si = 0.83. As the Ca/Si molar ratio increases, bridging tetrahedra in the dreierketten units (seen in Figure 6 linking silicate dimers to form dreierketten chains) are progressively removed.[9,10] Above Ca/Si = 1.3 sections of chains, or whole silicate chains, are removed from the structure to create jennite-like environments with Ca−OH bonds in the central layer.[12] These structural variations can be invoked to account for the differences in intercalation.

PVA intercalates the Ca^+-montmorillonite or $4CaO \cdot Al_2O_3 \cdot 11H_2O$ in a linear conformation to maximize hydrogen bonding with the layers.[7,8] The interlayer basal spacing in these structures must be increased substantially to accommodate the PVA molecules in this way (effective diameter 0.45 nm). In the case of C−S−H, one monomer unit of PVA is associated with one repeating sequence of the structure. Omission of sections of dreierketten at high Ca/Si ratios might create additional interlayer space that could accommodate extended linear PVA chains, lying between dreierketten and hydrogen bonded to Ca−OH groups, with only a slight increase in the basal spacing. This is shown schematically in Figure 7. Since chain omission is random, the flexible PVA molecule must be oriented

randomly in an extended 2-D conformation between the layers to minimize steric factors.

The larger layer expansion (1.3 nm) associated with the adsorption of PAA suggests an inability to fit between the dreierketten, probably due to steric effects of the carboxylate group. However, the maximum expansion exceeds that expected for bilayers of an extended comformation of the polymer chain (0.8–0.9 nm) on the basis of intercalation of small molecules.[5,7] The fact that 2.5 monomer units are adsorbed for each repeating unit of the C−S−H structure suggests that the polymer interacts with both layers simultaneously, as proposed for $4CaO \cdot Al_2O_3 \cdot 11H_2O$[5] and that unbonded loops may also be present. This would account for the broadened basal peak of the complexes and the fact that a limiting value for the interlayer spacing and carbon content is not attained, in contrast to the PVA complex.

Cationic PDC can only intercalate at lower Ca/Si ratios when most bridging tetrahedra in the dreier-ketten are in place. When this happens there is a high content of Si−OH groups in the interlayer region,[12] which appears to enhance the bonding with cationic functional groups of the polymer. The layer expansion is similar to that observed for diamines in $4CaO \cdot Al_2O_3 \cdot 11H_2O$[5] and occurs when one monomer unit adsorbs for each repeating unit of C−S−H.

Attempts to intercalate small organic molecules with similar functional groups (e.g. glycerol, propanediol, ethylene glycol, succinic acid, maleic acid) into C−S−H have not been successful, in contrast to $Ca_4Al_2O_8 \cdot 11H_2O$[5] and clay minerals. However gluconic acid (six carbons in the chain) did intercalate when Ca/Si = 1.3, giving a layer expansion of 0.37 nm. Therefore, it can be concluded that intercalation between C−S−H and polymers depends on an alignment between the two structures to optimize interactions between several functional groups and the C−S−H structure simultaneously.

C−S−H/polymer complexes have been synthesized for the first time in this study, and their formation opens up a potentially new route for the synthesis of nano-composites using layered hydrates and organic polymers. The variable C−S−H structure presents a unique opportunity to probe the factors that affect intercalation bonding. A study of intercalation of other water-soluble polymers is in progress, including whether "super-plasticizing" polymers, which are used to modify the flowability of cement and concrete, will form similar complexes with C−S−H formed from the hydration of calcium silicates in Portland cement.

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