

Cement-silylated polymers nanocomposites

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ABSTRACT

Inclusion of nanometer-wide polymer regions that covalently bond C-S-H crystallites should make crack propagation more difficult in cement-based materials. Interfacial energy and dissipative properties of soft matter should enhance tenacity and flexural strength.

We have studied C₃S hydration and C-S-H precipitation from salts with aqueous solutions containing silane-grafted polymer. Both the microstructure of resulting composites and the role of silane moieties have been studied.

Silane is necessary to covalently bond polymer chains to C-S-H. NMR CP-MAS and X-ray diffraction experiments on sol-gel composites confirm the covalent nature of silane/C-S-H bonds. Nanometer-wide polymer domains surround C-S-H crystallites, with no chains in the interlayer space. Each silylated polymer we tested behaves the same. C₃S sets rapidly, even in the presence of silane/C-S-H covalent bonds.

The microstructure and mechanical behavior of hydrated C₃S remains to be explored. This study will continue with nanocomposites based on silylated templates of an elastomer in aqueous solution.

I. INTRODUCTION

Association of inorganic entities and macromolecules in natural materials may lead to remarkable materials, regarding their mechanical properties such as strength, toughness or ductility. For example, alternation of hard and soft regions as in nacre [1], in which nanometer-thick organic films strongly bond aragonite platelets, should make crack propagation more difficult. In the opposite hydrated Portland cement is a brittle and stiff material. The flexural strength may be increased if a polymer like polyvinyl alcohol fills its largest pores [2][3], but a fracture resistance increase is not achieved. A better control of the polymer dispersion in the mineral matrix should be more efficient to increase resilience. In this sense, the optimization of interaction between hydrated cement crystallites and polymer is the first step to control the polymer dispersion. The main hydrated phase in Portland cement is a nano-sized layered crystal, named C-S-H. Each layer is composed of a distorted central Ca-O sheet and silicate chains. Interlayer space contains calcium ions and water molecules. Intercalation of ionic polymers within basal spacing of C-S-H is barely effective [4-10]. To increase interaction, the strategy used in this work was to replace electrostatic interactions between polymer and C-S-

H, by specific covalent ones. To reach that goal, we used hydrophilic polymers modified by silane groups able to be incorporated in the C-S-H framework. We have synthesized silylated polyvinylpyrrolidone (PVP) and polydimethylacrylamide (PDMA). We report here precipitation experiments of C-S-H in presence of these polymers, and NMR and XRD data of the nanocomposite. Influence of polymer on C₃S hydration has also been studied.

II. EXPERIMENTAL

II.1. Synthesis and protocols

II.1.a. Poly(vinylpyrrolidone-vinyltriethoxysilane) (PVP-Tn). The statistic copolymer has been obtained by radical polymerization of vinylpyrrolidone and vinyltriethoxysilane. This method has been described elsewhere [11][12]. (see Fig.1). Copolymer with different silane/pyrrolidone molar ratio (n%), between 0 and 23, was synthesized.

II.1.b. Poly-(N,N-dimethylacrylamide-3-(acryloxylamino)propylmethyl dihydroxysilane-3-(acryloxylamino)propyltrihydroxysilane (PDMA-Dm-Tn). A backbone of P(DMA-co-AA), AA for acrylic acid, was first synthesized by radical polymerization with a $M_w = 300\,000$ g/mol, $I_p = M_w/M_n = 2.5$, and 15 mol% of statistically distributed acid groups [13]. Silane groups has been grafted on this backbone by peptide coupling [12] (see Fig.2) using a mixture of 3-aminopropyltriethoxysilane (APTES) and 3-aminopropylmethyldiethoxysilane (APDES). APTES has three Si-O bonds (T- function), whereas APDES has two Si-O bonds and a methyl (D-function). In the polymer formula, n and m stand for the T and D molar percentage, respectively.

II.1.c. Polymer/C-S-H nanocomposites. Nanocomposite materials were prepared by a coprecipitation method derived from the C-S-H sol-gel protocol of Suzuki and Sinn [14], with an initial Calcium to Silicium ratio (C/S) of 0.83. A tetraethylorthosilicate (TEOS, 1.9 ml) and polymer (0-1g) mixture were dispersed in 5 ml of CaCl₂ (0.91 g) acid solution (HCl, pH=3). This solution was stirred during one hour, and then 10 mL of a 4M NaOH solution was dripped. The pH increase leads to precipitation. After a mixing time of 24 hour at 50°C, the precipitate was three times washed by centrifugation at 6000 rpm with 100 ml of distilled water, in order to remove polymer in excess. Composite was dried by lyophilization. Similar protocol was made with silane precursors APTES or APDES instead of polymers.

II.1.d. C₃S hydration. Synthetic C₃S was hand mixed with polymer solution. Dilute suspension of C₃S was prepared with w/c = 100, and concentrated ones with w/c = 0.4. These experiments were conducted with various amounts of polymer, at 25°C, in sealed containers.

II.2. Instrumentation

Nanocomposites were characterized by XRD (Philips PW1729 diffractometer - Cu -K_α radiation) and ²⁹Si NMR. NMR ²⁹Si (ASX500 Brücker spectrometer). Polymer amount precipitated in nanocomposite was determined by thermogravimetric measurements (TGA/TGD experiments with SDT 2960, TA Instrument under airflow with a heating rate of 10°C/min up to 1000°C). C₃S-polymer setting time was determined by ultra sonic reflectivity measurement (homemade generator of shear waves operating at 1MHz). The shear module variation with time was determined from the reflectivity coefficient at the interface between the C₃S paste and the waveguide. The amount of C-S-H precipitation during hydration of dilute C₃S-polymer suspension was deduced from the amount of precipitated portlandite, quantified by thermogravimetric measurements. BET specific surface area of C-S-H was measured from 50°C dried samples.

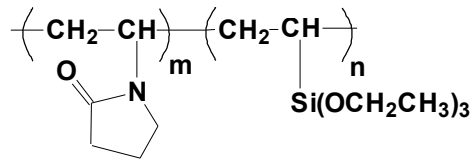


Fig. 1. PVP-Tn

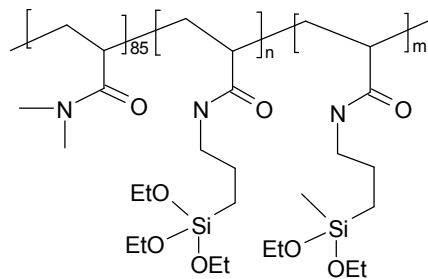


Fig. 2. PDMA-Dm-Tn

III. RESULT AND DISCUSSION

III.1. Nanocomposite with C-S-H and silylated polymer

III.1.a. Composition of nanocomposite. Materials obtained by coprecipitation of silane precursors (APTES or APDES) and C-S-H are mainly different. In the first case, large fraction of silane are incorporated with C-S-H in the solid phase, whereas in the second case, the precipitate is only composed of C-S-H. It appears that interactions between C-S-H and silane mainly depend on the silane nature (T or D). According to previous results [15][16], a co-precipitation of T-silanes, TEOS and calcium leads to the formation of hybrid structures. In such structures,

silanes insert into silica chains of C-S-H. Silane organic chain is located in the interlayer. In this case, the basal spacing of the hybrid rises with the length of the chain. The present experiment shows that D-silane are unable to bond C-S-H. It suggests that at least three Si-O bond are essential to insert silane into silicate chains.

Same trends are observed when silanes are grafted on polymer. Fig.3 shows thermogravimetric measurement (TGA) of precipitate obtained with D-silane grafted polymer (PDMA-D15-T0) and T-silane grafted polymer (PDMA-D0-T15). In the first case, the absence of mass loss associated to organic decomposition suggests no polymer incorporation in the material. In the second case, the mass loss at $\sim 360^\circ\text{C}$ confirms the presence of polymer in the material. It suggests again that the nature of silane is of primary importance.

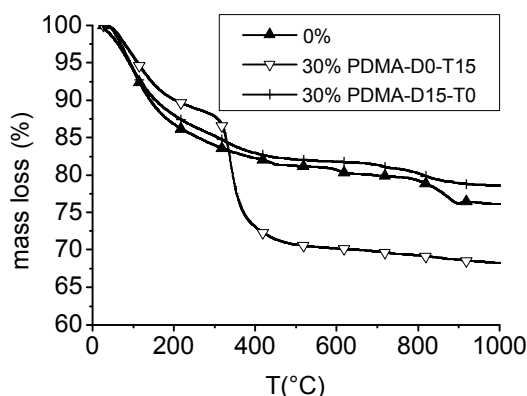


Fig. 3. Mass loss versus temperature for composite with PDMA-D0-T15 and PDMA-D15-T0.

For all nanocomposite studied, quantification of polymer amount in the precipitate was calculated from the mass loss of the TGA curves between 250°C and 450°C . Fig.4 shows the polymer amount in the nanocomposite in function of the initial polymer amount in the starting solution. For all polymer studied, only polymer containing T-silane groups are able to form nanocomposite. For large amount of polymer in the initial solution, we found less than 0.03 g of polymer by gram of C-S-H, for PDMA-D15-T0 and PVP-T0, and more than 0.2 g/g for all polymer containing T-silanes groups. 0.2 g of polymer of polymer in the nanocomposite per gram of C-S-H seems to be a maximal amount that can be reached even with large quantities of polymer in the solution.

Fig.5 shows the maximal value of polymer that can be incorporate in the nanocomposite vs. the nature of the polymer. This value appears to depend neither on the backbone nature nor on the T-silane percentage. For example, same quantity of polymer maybe incorporated in nanocomposite for PDMA-D13-T2 and PDMA-D0-T15. These results show the efficiency of triethoxysilane to form strong bonds with C-S-H.

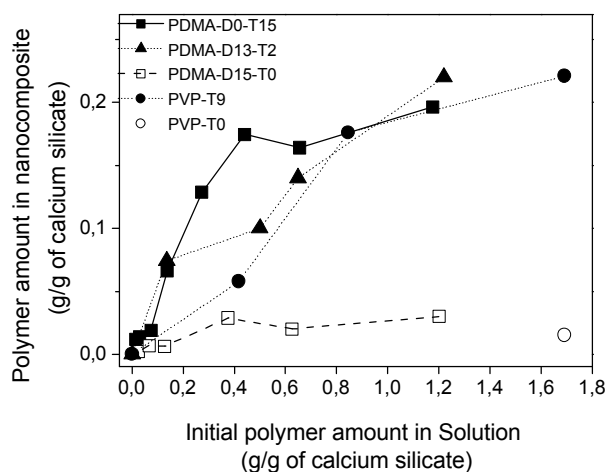


Fig. 4. Polymer amount in nanocomposite vs. initial polymer amount in solution.

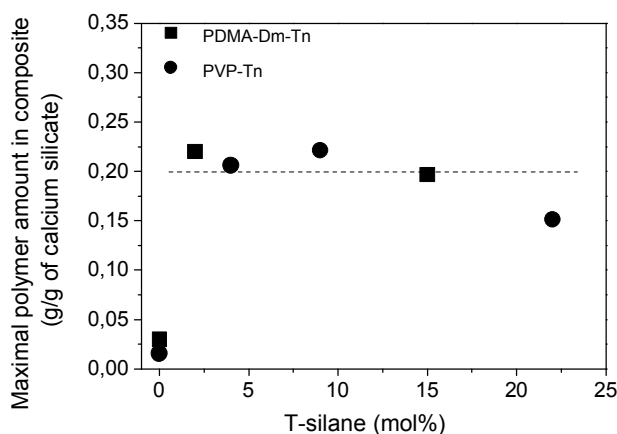


Fig. 5. Influence of the amount of T-silane functions grafted on the polymer on the maximum polymer content in precipitated composites. (initial polymer amount in solution > 1.2 g/g of calcium silicate)

III.1.b. Nanocomposite structure. ^{29}Si NMR experiments were conducted in order to investigate the T-silane/C-S-H bond nature. In Fig.6, ^{29}Si NMR spectra are reported for C-S-H and nanocomposite with T-silane polymers. Typical peaks of C-S-H are observed (-79 ppm and -85 ppm). These peaks are attributed to end- and mid-chain silica, Q^1 and Q^2 , respectively, which are typical of a C-S-H « dreierketten » structure [17] (Q^n stands for silicate species, T^n for silane species. n represent the number of Si-O bonds). Additional peak in nanocomposite spectra at about -50 ppm is assigned to T species^[16]. It confirms the presence of polymer in the nanocomposite. The low intensity of this peak is consistent with the low proportion of T-silane in the material. We then focus on the peak related to T species. Fig. 7 shows that the polymer alone (solid state) has two peaks at -58 ppm and -64 ppm typical of T^2 and T^3 species, respectively. In solid polymer a majority of silanes are condensed to form siloxane bonds. This configuration is different when the polymer is precipitated with C-S-H. In this case, only one peak at -50 ppm chemical shift is observed, which is typical of T^1 environment and means the silane

form only one siloxane bond. This difference suggests that the polymer is highly dispersed in the mineral phase, and does not segregate. Supplementary NMR experiments reported elsewhere^[16], have shown that T-silane specifically bonds silicate chains of C-S-H.

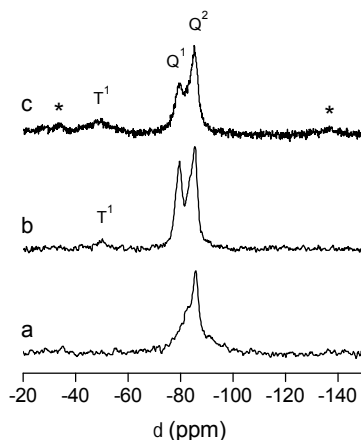


Fig. 6. ²⁹Si NMR spectra of a) C-S-H; b) PDMA-D0-T15/C-S-H composite; c) PVP-T9/C-S-H composite. *Peak due to spin rate.

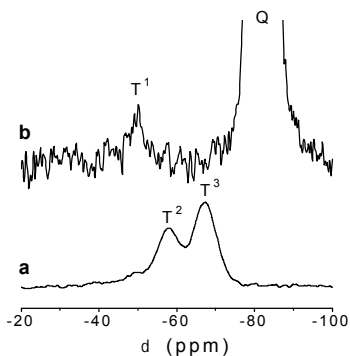


Fig. 7. ²⁹Si NMR spectra of a) PDMA-D0-T15 (solid); b) PDMA-D0-T15/C-S-H composite.

Fig. 8 shows the powder X-ray diffraction patterns of C-S-H and some examples of polymer/C-S-H composites. The diffraction diagram of the pure C-S-H material (fig. 8, a) is typical of relatively ordered C-S-H^[17]. At low angles, the observed diffraction peak is attributed to the (001) reticular planes, which are characteristic of the layered stacking. At higher angles, the set of diffraction peaks is attributed to the (hk0) reticular planes that are characteristic of the organisation of the calcium atoms within each C-S-H layer. When C-S-H is precipitated in the presence of polymers, in-plane hk0 reflections are unchanged, proving that the in-plane organisation of the calcium atoms is the same as in C-S-H. Nevertheless, the 001 basal reflection is broadened and decreases in intensity. This trend is reinforced as the amount of polymer in the starting solution is increased (compare in Fig. 8, b and c). For higher starting polymer

concentrations, this peak disappears (Fig. 8, e). This tendency is observed just as well with T-silane polymer and D-silane polymer. In all cases, the position of the basal peak does not evidence the intercalation of polymer. All of these results suggest that the regular stacking of the lamellas during precipitation is disturbed by the presence of the polymer, but is not related to the incorporation of the polymer inside the C-S-H interlayer.

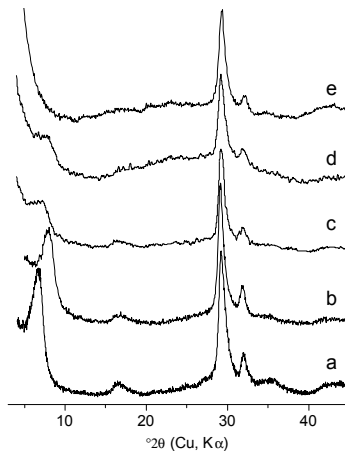


Fig. 8. Powder X Ray diffraction patterns of: (a) C-S-H, (b) PDMA-D15-T0/ C-S-H with an initial polymer amount in solution equal to 0.14 g/g, (c) PDMA-D15-T0/ C-S-H, 0.27 g/g, (d) PDMA-D0-T15/ C-S-H, 0.27 g/g (e) PVP-T9/C-S-H 1.7 g/g

The influence of the stirring time of PDMA-D0-T15 polymer and inorganic precursors at 50°C on the properties of composite materials was also studied. Fig. 9 shows that basal ordering increases with reaction time. Conversely, the amount of polymer precipitated in the solid phase decreases (Fig. 9 inset). Growth of C-S-H crystallites and, in consequence, decrease of BET surface area, is generally observed during reaction time between silicon and calcium precursors in aqueous suspension. At short times (few minutes), the BET specific surface is 150 m².g⁻¹ and the polymer amount is 0.08 g/g while at 12 days the specific surface area is 80 m².g⁻¹ and the polymer amount 0.048 g/g. The proportionality between specific surface and precipitated polymer confirms that polymer interacts only with the external surface of C-S-H crystallites.

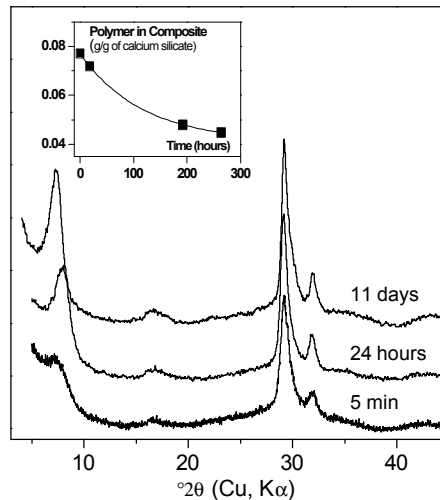


Fig. 9. Influence of mixing time of PDMA-D0-T15/C-S-H (initial polymer in solution = 0.27 g/g of calcium silicate) on XRD patterns. Inset: polymer amount precipitated in hybrid vs. mixing time.

III.2. C₃S/polymer hydration

Hydration of C₃S in presence of polymer has been studied in diluted suspension (w/c=100) and concentrated paste (w/c=0.4).

In the first case, low amount of C₃S is suspended in polymer saturated solutions (polymer concentration in the solution p/w= 0.02, w/c=100). The solid phase is analysed by TGA after four days, to evaluate the portlandite amount. The mass loss associated to Portlandite is endothermic and centered on 460°C. Large amount of portlandite are found after 4 days in both T-silane free polymer/C₃S suspension and in pure C₃S suspension (41% and 37%, of the Portlandite amount at maximal hydration, respectively). It is consistent with the lack of interaction between D-silane and C-S-H. As the T-silane fraction increases, the amount of precipitated portlandite decreases, suggesting a slower hydration (10% with PDMA-D13-T2). No hydration occurs with PDMA-D0-T15 (less than 0.5% of the portlandite amount at maximal hydration).

Same behaviors are observed for the setting times of concentrated paste (see Fig.10). This figure represents the shear modulus measured by ultrasonic wave reflection. The samples are composed of C₃S, water and PVP with and without T-silanes. Polymer amount is 0%, 0.2% and 1% with respect to the C₃S, w/c=0.4. The modulus reaches a first plateau (around 1 MPa) during the induction time, and then reaches a second plateau (around 10 GPa) as the paste set. As the amount of T-silane in the paste increases, a significant lengthening of the induction time is observed. Once C₃S is set, shear modulus reaches the same order of magnitude for all samples. From these experiments in concentrated paste and diluted suspension, it may be concluded that T-silane functions (but not D-silane) strongly retard C₃S hydration. The retarding process is probably due to strong adsorption of T-silane on C₃S surface.

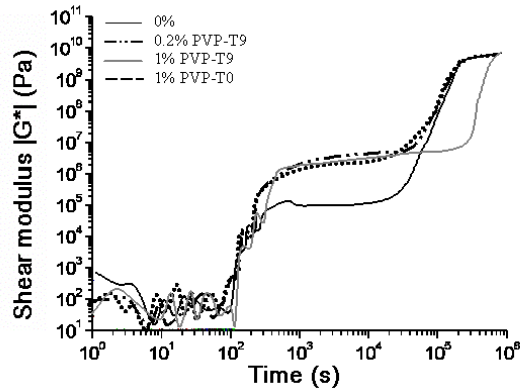


Fig. 10. Shear modulus vs. time for several polymer/cement ratio

CONCLUSION

- Hydrosoluble copolymer grafted with trialkoxysilane and/or dialkoxysilane has been synthesized.
- Precipitation of C-S-H in presence of silylated polymer has been studied. Only T-silane grafted polymer are able to interact with C-S-H. A small amount of these silane is sufficient to strongly bond the polymer to C-S-H.
- Nanocomposite has been characterized by XRD and ^{29}Si NMR. We have found that polymer does not insert in the crystallite interlayer.
- These T-silane groups mainly retard C_3S hydration.

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