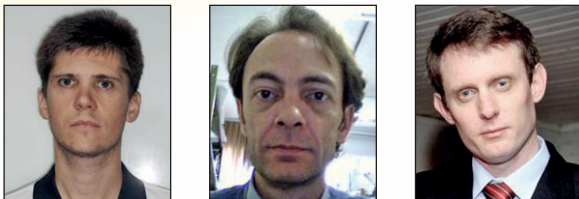# Synthesis of calcium silicate hydrate/polymer complexes

Síntese de complexos de silicato de cálcio hidratado/ polímeros

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Abstract

Hydrated cement paste, composed for the most part by calcium silicate hydrate (C-S-H), is a fragile material with low tensile strength. It is also well known that the addition of silica fume to concrete increases its strength and, consequently, makes it more durable, though also more fragile. To produce more ductile C-S-H, one alternative is the synthesis of C-S-H/polymer nanocomposites or hybrids. The intercalation of organic molecules in C-S-H nanostructure and other cement hydrates can promote radical changes in their properties of all magnitudes, producing cement based materials with greater strength that are also more ductile. The main objective of this work was to study the possibility of intercalation of organic compounds within C-S-H nanostructure, aimed at the synthesis of nanocomposites with atypical properties. Thus, C-S-H gels were synthesized with various Ca/Si molar ratios using two synthesis methods (precipitation synthesis and pozzolanic synthesis), with or without the presence of polymers. The effect of poly-diallyldimethylammonium chloride (PDC - used as the basis for superplasticizers for concrete) was evaluated, indicated by the literature as capable of intercalating between the C-S-H lamellae [1-5], and copolymer poly(ethylene-co-vinyl acetate) (EVA), indicated by the literature as a modifier of C-S-H morphology [6,7]. The PDC polymer promoted alterations in C-S-H synthesis nanostructural bonding, influencing the interlayer distance and the type of bonding in the dreierketten and wollastonite chains. However, this modification was partial and occurred at rates that require further investigation, since they are probably influenced by the complex characteristics of formation, both by the type of bond and by the irregular and minimally crystalline formation of C-S-H.

Keywords: C-S-H, nanostructure, polymers.

Resumo

O cimento hidratado, composto majoritariamente por C-S-H, é um material frágil com baixa resistência à tração. Sabe-se também que a adição de sílica ativa ao concreto torna-o mais resistente e, conseqüentemente, mais durável, mas, em contrapartida, ainda mais frágil. Para tornar o C-S-H mais dúctil, uma alternativa é a fabricação de nanocompósitos ou híbridos C-S-H/polímero. A intercalação de moléculas orgânicas na nanoestrutura do C-S-H e de outros hidratos do cimento pode ocasionar mudanças radicais das propriedades em todas as ordens de grandeza, produzindo produtos cimentícios mais resistentes e também mais dúcteis. O principal objetivo deste trabalho é avaliar a possibilidade de intercalação de compostos orgânicos na nanoestrutura do silicato de cálcio hidratado (C-S-H), principal composto de hidratação do cimento Portland, visando a formação de nanocompósitos com propriedades diferenciadas. Para isso, foram sintetizados géis de C-S-H com varias relações molares Ca/Si a partir de dois métodos (síntese por precipitação e síntese pozolânica); sem e com a presença de polímeros. Foram avaliados os efeitos do poli-cloreto de dialilmetilamonia (PDC-utilizado na fabricação de super-plastificantes), apontado pela literatura como capaz de se intercalar no espaço interplanar do C-S-H [1,2,3,4,5], e do copolímero acetato de vinila/etileno (EVA), apontado pela literatura como modificador da morfologia do C-S-H [6,7]. O polímero de PDC propiciou alteração na ligação nanoestrutural do C-S-H de síntese, influenciando na distância interplanar e no tipo de ligação na região de dreierketten e wollastonita, porém esta modificação é parcial e em taxas que ainda devem ser investigadas, as quais são provavelmente influenciadas pelas características complexas de formação - quanto ao tipo de ligação - e pela formação aleatória e pouco cristalina do C-S-H.

Palavras-chave: C-S-H, nanoestrutura, polímeros.

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1. Introduction

The aim of nanotechnology is to create new materials and develop new products and processes based on the increasing power of modern technology to observe and manipulate atoms and molecules. Energy saving, environmental protection and reducing the use of scarce raw materials are possible applications of nanotechnology.

Portland cement is the most common material used in construction; consequently, cement nanotechnology and its products are of great importance to this industry. Hydrated cement is composed mainly of a calcium silicate hydrate commonly called C-S-H[1]. During hydration, C-S-H progressively covers the grains of anhydrous cement and slowly fills the intergranular space, forming complex nanostructures. This hydrated phase, considered the true ligand of hardened cement paste and is primarily responsible for most of the properties of hardened cement paste [9]. The cohesion of the C-S-H matrix depends on the bonding scheme forces of the intralamellae sheets (interlayer spacing), classified as nanostructures, together with the solid-solid bonds between lamellae stacks (interlamellae) and water adsorbed on the surface, classified as bonds in the mesostructure [10].

Applying the concepts of nanoscience in cement-based materials could lead to improved control of the microstructure and, for example, improved cohesion and flow, avoiding problems of cracking at early ages, gains in strength at increased velocity, reduced permeability and the consequent increase the durability of materials and improvement in cement performance [11].

Most advances in the performance of cement materials achieved in recent decades are due to the optimization of granular stacking and, particularly, the reduction of capillary porosity with rational use of increasingly efficient chemical additives. However, in terms of efficiency, such advances are close to an asymptote, which suggests that further improvement of mechanical properties can only come from modifications of finer material scales. The interest in nanocomposite materials, organic and inorganic, has emerged from this finding. Nature itself has developed a fantastic and great diversity of organisms that take advantage of this synergy: including shells, bones and teeth. These materials exhibit unique properties in terms of toughness and flexural strength, among other parameters, and ahieve this at extremely low organic levels. Knowledge and the reproduction of strategies associating the organic and inorganic phases used by nature open up diverse perspectives regarding the manufacture of synthetic materials with unusual properties [9].

Consequently, a potential solution to make C-S-H more ductile is the manufacture of C-S-H/polymer nanocomposites. The intercalation of organic molecules within the C-S-H nanostructure and other cement hydrates permits potential changes in their properties at all orders of magnitude.

The first C-S-H/polymer nanocomposites were synthesized by Matsuyama and Young [1-5]. The authors reported the intercalation of polymeric groups of additives for concrete between the interlayer of C-S-H. They affirmed that the success of intercalation depends on the nature of the ionic groups (cationic, anionic, neutral) of the polymer and the Ca/Si molar ratio of C-S-H. In some of the compounds obtained, the authors verified significant increases in carbon content and the basal distance d_{002}, suggesting the incorporation of polymeric groups between the interlayer of C-S-H. Thus, they observed that anionic polymers were intercalated in C-S-H with a high Ca/Si (> 1) ratio, while cationic polymers were intercalated in C-S-H with a low Ca/Si (<1) ratio. However, this conclusion is controversial; Popova et al. [12] did not observe intercalation, rather the adsorption of polymers in C-S-H. However, the authors used a method of C-S-H synthesis different to that of Matsuyama and Young [2-5]. According to Merlin et al. [10], the polymers are not inserted into the interlayer spaces of C-S-H, but settle on the surface of the gel pores (adsorption). However, so far, the hypothesis proposed by Merlin et al. [10] has not been proven.

In this study, calcium silicate hydrates were synthesized in accordance with the recommendations of Matsuyama and Young [2-5] and Gmira [13], in order to evaluate the interaction of poly(diallyldimethylammonium) chloride (PDC) and the copolymer poly(ethylene-co-vinyl acetate) (EVA) on the nanostructure of C-S-H. According to the results reported by Matsuyama and Young [4.5], PDC intercalates in the nanostructure of C-S-H. However, these results were not confirmed in research by Merlin et al. [10], who observed a modest expansion in the interlayer distance (0.2 nm for Ca/Si = 0.9 /PDC) using the precipitation synthesis process and, surprisingly, a carbon content of 10% compared to the cement mass, equal to the results of Matsuyama and Young [3-5]. Merlin et al. [10] attributed these results to adsorption of the polymer on the surface of C-S-H. In the case of EVA, the literature indicates that it interacts chemically with cement hydration products, which can modify the nanostructure of C-S-H [6,7].

Table 1 – The Ca/Si molar ratio of C-S-H produced by pozzolanic synthesis (Mixing time: 70 days - Drying time: 14 days) and precipitation synthesis (Mixing time: 14 days - Drying time: 14 days)

	Mixtures	Ratio Ca/Si planned	Ratio Ca/Si mixed
Pozzolanic method	C-S-H	0.70	0.77
	C-S-H+PDC[1]	0.70	-
	C-S-H+EVA[2]	0.70	-
	C-S-H	0.90	-
	C-S-H+PDC	0.90	-
	C-S-H+EVA	0.90	-
	C-S-H	1.20	1.20
	C-S-H+PDC	1.20	-
	C-S-H+EVA	1.20	-
Precipitattion	C-S-H	0.60	0.56
	C-S-H+PDC[1]	0.60	0.56
	C-S-H	0.80	0.62
	C-S-H+PDC	0.80	-
	C-S-H	1.00	0.78
	C-S-H+PDC	1.00	-

[1] Polymer concentrations PDC were 42.5 g/L (4).
[2] Polymer concentrations EVA were 10g/L.

[1] C-S-H is considered a lamellar, crystalline semi-continuum and inherently complex material, particularly in relation "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 [8].

2.   Materials and methods

2.1   C-S-H synthesis

C-S-H was produced with varying Ca/Si ratios using two methods, precipitation synthesis and pozzolanic synthesis, with and without the presence of PDC and EVA polymers.

2.1.1 Pozzolanic synthesis

The process of C-S-H formation by pozzolanic synthesis [12, 13] is achieved by the reaction of CaO (obtained after calcination of pure $CaCO_3$ for 2 h at 1100°C) with silicic acid in the presence of deionized water. The Ca/Si ratio was a variable controlled and maintained at 0.7, 0.9 and 1.2, according to the mix design shown in Table 1, while maintaining the water/solid ratio constant at 20. After the initial mixing, the material was placed in a water bath with a stirring system and a constant temperature of 60°C for 70 days. The products obtained were filtered and dried in a vacuum oven at a temperature of 60°C for 14 days [13]. Once dried, they were ground in an agate mortar, passed trhough a 75 μm sieve and submitted for analysis. Table 2 shows the main characteristics of materials used.
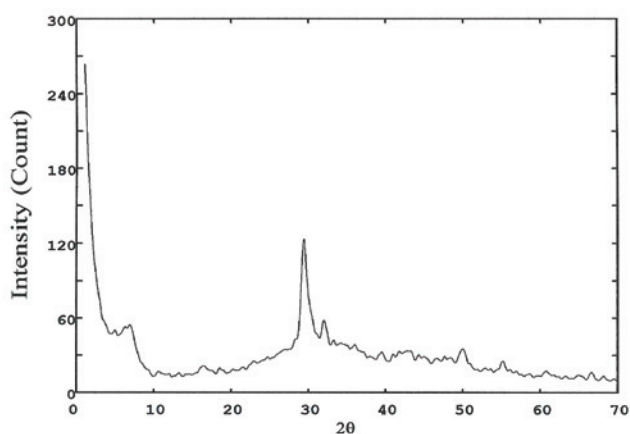
2.1.2 Precipitation synthesis

Precipitation synthesis of C-S-H consisted of the gradual addition of

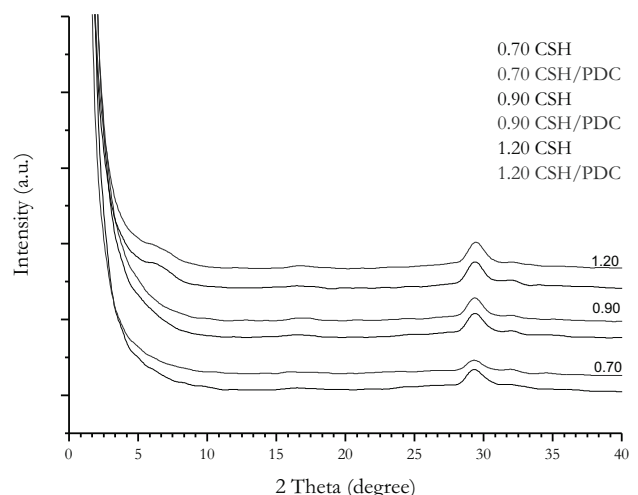| Table 2 – Characteristics of the materials used in pozzolanic and precipitation synthesis		
Calcium Carbonate	Composition	$CaCO_3$
	Producer	Sigma-aldrich
	Mol wt	100.09 g/mol
	Density	2.93 g/mL
	Total impurities	<0.00005%
Silicic Acid	Composition	H_2SiO_3
	Producer	Sigma-aldrich
	Particle Size	20μm
	Purity	>99.9%
Calcium Nitrate Tetrahydrate	Composition	$Ca(NO_3)_2.4H_2O$
	Producer	Sigma-aldrich
	Mol wt	236.15 g/mol
	Total impurities	<0,00005%
Sodium metasilicate nonahydrate	Composition	$Na_2SiO_3.9H_2O$
	Producer	Sigma-aldrich
	Mol wt	284.20 g/mol
	Properties	SiO_2 = 44-47%
Poly-diallyldimethylammonium chloride-PDC	Composition	(C8H16ClN)n
	Producer	Sigma-aldrich
	Mol wt	100,000 – 200,000 g/mol
	Density	1.04 g/mL
	Viscosity	60-80 cP
Poly(ethylene-co-vinyl acetate) redispersible polymer powder -EVA1	**Characteristics of powder**	Protective colloid	Poly(vinyl alcohol)
		Content of solids (thermogravimetric)	99±1%
		Content of inorganic	7.63%
		Apparent density	1.34 g/cm^3
		Particle size	11% acima de 250μm
		Glass transition temperature (Tg)	11.2°C
	Characteristics of the particle made from the powder	Particle size	1 a 8 μm
		Minimum film forming temperature	Aproximadamente 4°C

[1] EVA redispersible polymer powder was used VINNAPAS^R RE5010N (Wacker) and the characteristics were obtained in SILVA (14) and producer (Wacker).

Figure 1 – X-ray diffraction diagram of synthesized tobermorite: plane (002) (14 Å) around 6.5° (2θ); plane (220) (3.06 Å) around the 30° (2θ); plane (200) (2.81 Å) around 32.5° (2θ)

Figure 2 – X-ray diffractogram of C-S-H produced by pozzolanic synthesis with varying Ca/Si ratios, with and without poly (diallyldimethylammonium)chloride (PDC)

a calcium nitrate solution (1 mol/L), while stirring, to a solution (0.22 mol/L) of sodium metasilicate with and without the presence of polymers (Table 1). The pH was maintained constant (between 13.1 and 13.3) by the addition of NaOH during the precipitation of C-S-H [2-5]. After 14 days at 60°C, the precipitate was filtered and washed with acetone and distilled water to remove sodium and nitrate ions and the fraction of the additive that was not incorporated into the C-S-H. Then the precipitate was dried in a vacuum oven at 60°C for 7 days. During this initial drying, small irregular clusters of C-S-H were formed, which were ground in an agate mortar, followed by drying up to 14 days. Once dried, the C-S-H clusters were ground in a micro-mill, with an agate mortar, passed through a 75 µm sieve and submitted for analyses. Mixtures were produced with varying Ca/Si ratios (0.6, 0.8 and 1.0; Table 1) in order to obtain true Ca/Si ratios below 0.8 to facilitate the intercalation of cationic polymers [4,5]. Pure C-S-H and C-S-H

with the addition of PDC were produced. The main characteristics of the materials used are presented in Table 2.

### 2.2 Characterization of the products obtained

To verify polymer intercalation between the interlayer spacing of C-S-H, X-ray diffraction (XRD) and infrared spectroscopy (FT-IR) were used. The ratios of Ca/Si were determined using chemical analysis by X-ray fluorescence. Analysis by X-ray diffraction was performed using X-Pert Philips equipment, which operates with CuKa radiation (λ = 1.5418 Å) and 30mA and 40kV of power. The scan was performed from 2° to 10° (2θ) at intervals of 0.02° and a reading time of 5s. The sample for the infrared spectroscopy assay was prepared by pressing the material into a pellet shape, using a proportion of 95% potassium bromide (KBr) and

Table 3 – Detection of the peak corresponding to the interlayer space "d" (Å) of the basal plane (002) of the compounds using X-ray diffraction

Mixtures	Ca/Si molar ratio		
	0.7	**0.9**	**1.2**
	Interlayer spacing "d" (Å) basal plane (002) 1 -10° (2θ)		
C-S-H	13.98 (very weak)	13.33 (very weak)	13.79 (weak)
C-S-H*	-	-	14.00 (strong)
C-S-H/PDC	13.99 (very weak)	17.90 (very weak)	12.9 (very weak)
C-S-H/PDC	13.90 (very weak)	not detected	14.03 (weak)
C-S-H/EVA	not detected	13.86 (very weak)	14.04 (weak)
C-S-H/EVA*	-	-	13.99 (strong)
* Grounded twice.			

**Figure 3 – X-ray diffraction of 0.6 C-S-H with the addition of PDC**
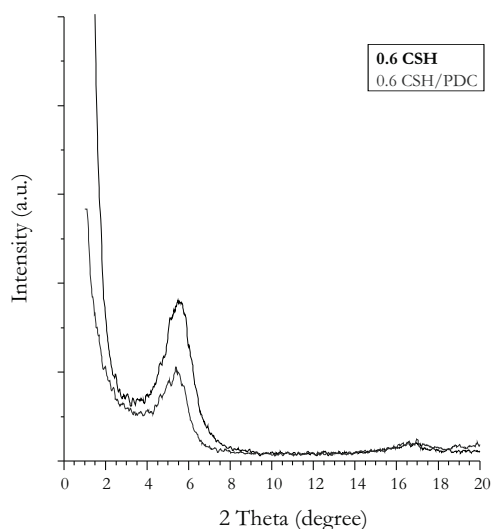
5% analysis material. The pressing load for the 13mm diameter pellet was 9 tons. The equipment used was a Shimadzu Privilege model. The analysis was performed by transmittance, at a speed of 0.2 cm/s and a resolution of $4cm^{-1}$, with a range of 400 to $4000cm^{-1}$.

3. Results and discussion

3.1 Pozzolanic synthesis

XRD analysis (Figure 1) verified the formation of calcium silicate

Figure 4 – X-ray diffraction of 0.8/1.0 C-S-H with the addition of PDC
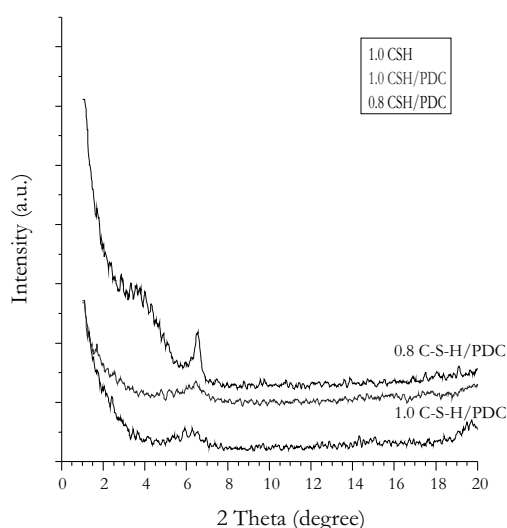
hydrate in the form of tobermorite 14 Å, with its main peaks: d_{220}, d_{002} and d_{200}, around 3.06, 14, and 2.81 Å, respectively.

In the majority of cases, the peak corresponding to the basal plane [002] was very weak and poorly defined, as observed in Figure 2 and presented in Table 3, due to the low crystallinity of the product. Table 3 also shows that the degree of milling seems to be a decisive factor for detecting the peaks.

Analysis of the results revealed no evidence of the intercalation of PDC or EVA in the basal plane [002] of C-S-H, in disagreement with the results obtained by Matsuyama and Young [4, 5] regarding PDC. An exception occurred concerning PDC for a Ca/Si ratio of 0.9, for which a small peak was observed at around 5° (2θ), corresponding to an interlayer spacing of 17.9 Å. The formation of C-S-H by pozzolanic synthesis is a slower process and may not have been satisfactory; however, in their studies involving nanocomposites, Matsuyama and Young [2-5] used the precipitation synthesis process evaluated in the following item.
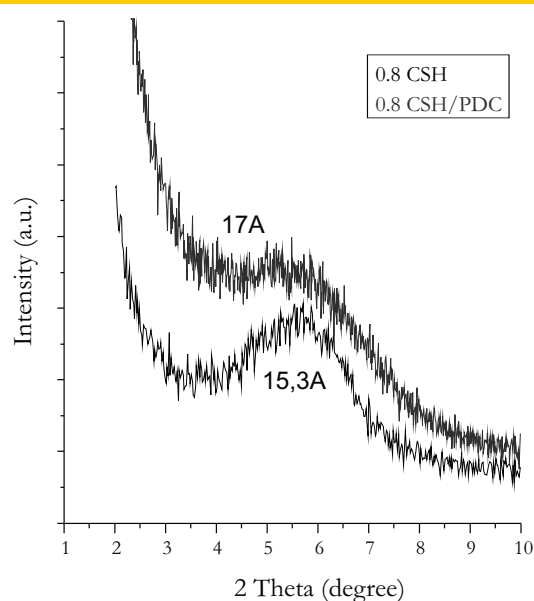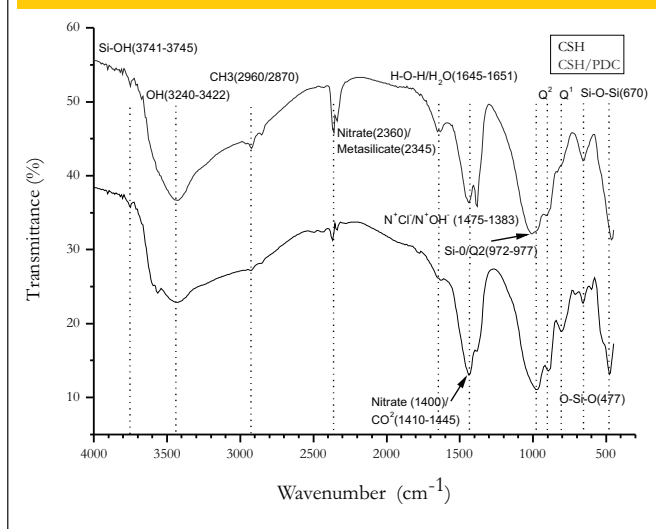
3.2 Precipitation synthesis

C-S-H was produced with varying Ca/Si ratios that were maintained below 0.8 to facilitate the intercalation of cationic polymers [4,5]. Analysis of the results verified the formation of calcium silicate hydrate similar to tobermorite 14 Å (for the basal plane d_{002}), as observed in Figures 3, 4 and 5, with a peak at approximately 14 Å.

Figure 3 shows that no modification occurred in the interlayer spacing with the addition of PDC to C-S-H produced with a Ca/Si molar ratio of 0.8 (0.62 by chemical analysis); thus, showing no evidence of PDC intercalation in the basal plane [002], contradicting the results of Matsuyama and Young [4.5].

However, when observing the X-ray diffractogram for C-S-H/PDC with a Ca/Si ratio of 0.8 (0.62 by chemical analysis) (Figure 4), this revealed the

Figure 5 – X-ray diffraction C-S-H produced with the addition of PDC

Figure 6 – FT-IR of C-S-H with and without the addition of PDC

the number of structural units linked together) was verified in the bands identified at 972 cm^{-1} and 895 cm^{-1} for C-S-H [15] and 998 cm^{-1} and 902 cm^{-1} for C-S-H/PDC. The most important difference was observed in the 802 cm^{-1} band in C-S-H regarding the Q^1-type bond, which is almost nonexistent in C-S-H/PDC.

According to Matsuyama and Young [4], the Q^2/Q^1 ratio that indicates the degree of polymerization in the *dreierketten* region is increased in the presence of polymers. Using nuclear magnetic resonance analysis (^{29}Si NMR), Matsuyama and Young [4] verified the presence of peaks at -79.8 ppm and -85.5 ppm for C-S-H, corresponding to Q^1 and Q^2-type Si-O, respectively. In the C-S-H/PDC nanocomposite, absence of a peak for the Q^1-type bond was verified. This kind of analysis was also performed by Popova et al. [12], who despite having used the pozzolanic synthesis method, observed no significant differences following the addition of polymers. The set of results presented, XRD and FT-IR, seems to confirm the intercalation of PDC within the interlayer spacing of C-S-H and the formation of a nanocomposite. Analyses conducted using the nanoindentation technique showed a reduction in the mechanical properties of C-S-H/PDC, which, together with images of the morphology obtained by transmission electron microscope [16], confirm the nanostructural alterations of C-S-H/PDC. A micrograph of the nanocomposite produced is presented in Figure 7.

4. Conclusions

The main results concerning the nanostructural alterations of C-S-H modified with synthetic polymers are presented below:

- The precipitation synthesis process was more efficient for C-S-H production;
- Observation verified that the addition of PDC led to partial modification of the interlayer spacing of C-S-H, which increased from 1.40 nm to 2.16 nm. Although, for the same mixture (C-S-H/PDC), the formation of a phase with an interlayer spacing of 1.4 nm has also been observed, thereby indicating the presence of two phases;

Figure 7 – Micrograph of C-S-H/PDC showing the site of a nanoindentation test (16)

formation of tobermorite 14 Å showing a characteristic peak at 6.5°(2θ) and another peak at 4.1°(2θ), confirming an increase in the interlayer spacing of 21.6 Å. This result coincides with the interlayer spacing observed by Matsuyama and Young [4.5], which they verified for C-S-H synthesis modified with PDC, showing an interlayer spacing of 21 Å.

Carbon content analysis showed an increase of 1.20% for C-S-H without polymer (in agreement with the results of Matsuyama and Young [4], 1.10%) and 2.65% for C-S-H/PDC, indicating partial fixation of the PDC. Considering the quantity of material added and the carbon content of PDC, the maximum carbon concentration possible in C-S-H/PDC could be 18%. The results obtained by Matsuyama and Young [4] presented a carbon content of 10% for C-S-H/PDC, suggesting intercalation of the polymer; whereas the results reported by Merlin et al. [10], who also determined a carbon concentration of 10%, permitted the author to conclude that adsorption of the polymer occurred, since other results (XRD) revealed no alteration in the interlayer spacing.

The results of this study suggest the partial formation of a C-S-H/PDC nanocomposite. A new series of mixtures were prepared and the results revealed a small increase in the interlayer spacing evaluated for C-S-H/PDC of 17 Å (Figure 5), similar to the values obtained by Merlin et al. [10]. For the latter combination the carbon content was determined as 5%.

Considering these results, the formation and the bonding structure of C-S-H should be considered random and irregular, which, according Pellenq et al. [8], would make polymer intercalation, when it occurs, difficult to achieve consistently.

The presence of the polymer was determined by FT-IR analysis, where in PDC is clearly identified in the bands 2970 cm^{-1} (CH3) and 1474/1381 cm^{-1} (N^+Cl^-) [4]. Type OH bonds were observed in C-S-H and C-S-H/PDC at 3433 cm^{-1} (Figure 6). However, differences between C-S-H/PDC and C-S-H were observed in the region between the interlayer in the Si-O-Si-type bonds; i.e., for both C-S-H and C-S-H/PDC, the presence of bonding in Q^2-type silicates (where Q^n represents the silica tetrahedron and n or 2,
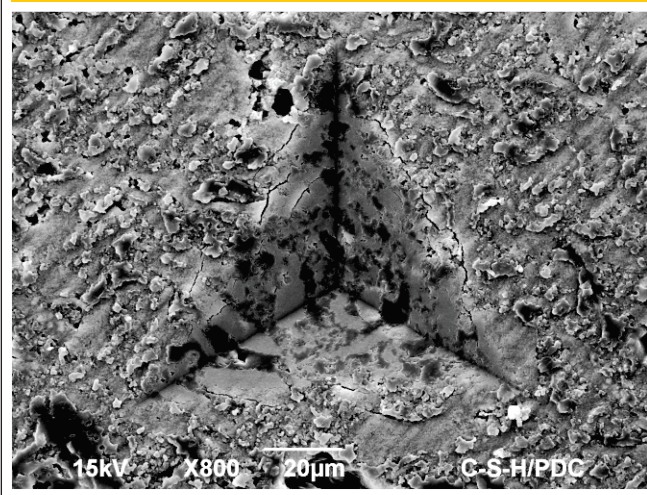
■ Using FT-IR analysis, the presence of PDC was observed, as well as an alteration in the type of Si-O-Si bonding between the interlayer spacing of C-S-H. For C-S-H, Q^1 and Q^2-type bonds were verified, while for the compound C-S-H/PDC, only Q^2-type bonds were verified, indicating a higher degree of polymerization of the *dreierketten* chains caused by the polymer and low quantities of free silica in the same region.

The results presented seem to confirm the intercalation of PDC within the interlayer spacing of C-S-H and the formation of a nanocomposite. These results contribute to the development of cement/polymer nanocomposites with distinct characteristics.

5. Acknowledgements

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