

Thermogravimetric Analyses and Mineralogical Study of Polymer Modified Mortar with Silica Fume

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Mineral and organic additions are often used in mortars to improve their properties. Microstructural investigation concerning the effects of styrene acrylic polymer and silica fume on the mineralogical composition of high-early-strength portland cement pastes after 28 days of hydration are presented in this paper. Thermogravimetry and derivative thermogravimetry were used to study the interaction between polymers and cement, as well as the extent of pozzolanic reaction of the mortars with silica fume. Differential scanning calorimetry and X ray diffraction were used to investigate the cement hydration and the effect of the additions. The results showed that the addition of silica fume and polymer reduces the portlandite formation due to delaying of Portland cement hydration and pozzolanic reaction.

Keywords: *silica fume, polymer, thermal analysis, X ray diffraction*

1. Introduction

Nowadays polymer modification of cementitious materials is frequently used in specific situations, where high performance towards durability, adhesion with substrates, or waterproofing properties is required. Pozzolanic materials can partially substitute Portland cement in order to enhance the properties of concrete and mortars such as durability and mechanical properties.

Polymer modified mortars are known as a popular construction material because of their excellent performance. The fundamentals about polymer modification for cement mortar and concrete have been studied for the past 80 years or more. Cement mortar and concrete made by adding polymer-based admixtures are called polymer-modified mortar (PMM) and polymer-modified concrete (PMC), respectively^{1,2}.

Polymeric admixture, or cement modifier, is defined as an admixture which consists of a polymeric compound that acts as a main ingredient in modifying or improving properties such as strength, deformation, adhesion, waterproofing and durability of mortars and concretes. Polymer latex is a colloidal dispersion of small polymer particles in water, which is obtained by emulsion polymerization of monomers with emulsifiers^{3,4}.

The literature agrees that the properties of polymer-modified mortar and concrete depend significantly on the polymer content or polymer-cement ratio, that is, the mass ratio of the amount of polymer solids in a polymer-based admixture to the amount of cement in a polymer-modified mortar or concrete^{1,2,5}.

There are two proposed theories of action for polymer in concrete^{6,7}. According to the first theory, there is no interaction between the polymer and cement, therefore during hydration the hydrophilic part of the polymer is oriented towards the water phase whereas the hydrophobic part head towards the air phase. The water is dried out in the setting phase, the polymer particles coalesce and build up a monolithic matrix phase with a network structure in which the hydrated cement phase and polymer phase interpenetrate into each other. The second theory is that the polymer interacts with the Portland cement hydration products and forms complexes.

The action of the saturated $\text{Ca}(\text{OH})_2$ solution on the surface of the set styrene-acrylate dispersion was studied^{6,8,9}. On the other

hand, the behavior of individual Portland cement components with polymers was found to be different when they are present together in cement. However, the mechanism of the interaction considering all the components of Portland cement acting simultaneously and polymers is not clear yet and discrepancies still exist⁶.

Silica fume or microsilica is an industrial by-product from an electric arc furnace producing silicon and ferrosilicon alloys. It has been widely used as a concrete and mortar mixture, mainly to improve the mechanical properties and reduce porosity, due to pozzolanic activity^{10,11}.

Finely ground material such as silica fume can increase the water required for a given degree of workability at low water-cement ratio, thus water reducing admixture (or superplasticizer) is often used to improve the workability of mortars with silica fume¹⁰.

Taking this into account, the correct combination of silica fume, superplasticizer and polymeric additions may have the synergistic effects of these three admixtures, resulting in the construction material performing well in specific applications, for example, high quality repairing and overlaying materials when applying concrete structures¹²⁻¹⁴.

In previous work, the authors studied the effects of silica fume and acrylic polymer on mortar properties, specifically to install porcelain tiles¹⁴. The mentioned work showed the improvement of adherence strength of mortars using such additions. Therefore, the aim of this work is to investigate the influence of such admixtures concerning the hydration of Portland cement by means of the mineralogical study of pastes with the same composition used in the work¹⁴.

The interaction between additions and cement portland can be investigated by various techniques such as thermal analysis and X ray diffraction. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) are considered important tools to evaluate the nature of hydrated products according to different stages of cement hydration, in addition to quantifying the different phases¹⁵⁻¹⁸.

When cement is hydrated, its main components are transformed into hydration products, mainly calcium silicate hydrate (C-S-H) and

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portlandite. The hydration can be evaluated by measuring the mass loss of hydrated compounds up to 900 °C. The following peaks and temperature ranges have been studied when hydrated cement is heated in thermobalance^{16,17}.

This study reports the results of investigations in which methods of thermal analysis, TG, DTG and DSC were applied to investigate the effects of polymer modification on the process of hydration of Portland cement by estimating Ca(OH)₂ content and C-S-H content. X ray diffraction was carried out to study the hydrate products of cement¹⁹.

2. Materials

2.1. Cement and silica fume

The mortars were prepared using high-early-strength Portland cement (CPV-ARI Plus) according to NBR 5733; and Type III cement according to ASTM C150). Chemical and physical properties of cement are shown in Tables 1 and 2, respectively, according to the manufacturer. The silica fume used was provided by Microsilica Brazil, with a specific surface area of 27.74 m²/g obtained by the BET test, and 94.3% SiO₂ content. Table 3 shows the chemical properties of silica fume, according to the manufacturer.

2.2. Superplasticizer

The superplasticizer, provided by MBT Brazil I. C., was used presenting chemical base sulfonated melamine, liquid aspect, density 1.11 g/cm³ (± 0.02), pH: 8.5 ± 16.49% solids content.

2.3. Polymer latex

- Aqueous dispersion of styrene-acrylate copolymer with 49% to 51% total solid content; Viscosity Brookfield (RVT 415 °C): 1000-2000 mPas; Density: 1.02 g/cm³; pH value: 4.5 a 6.5;
- Minimum film-forming temperature: 20 °C;
- Mean size of particles: 0.1 µm;
- Film properties: Clear and transparent; and
- Stability to ageing: good.

3. Experimental Program

Six mixtures were prepared as described in Table 4, which are the pastes with the same proportions used in the previous work¹⁴. The materials were weighed and mixed in a planetary-type mortar mixer. The total quantity of water was maintained, taking into account the water from the latex. The superplasticizer was also added in the ratio of 1% of the weight of cement.

The preparation of the samples for TG, DSC and X ray diffraction was carried out using an agate mortar and pestle, in which the paste was manually ground until the size of particles was lower than 0.063 mm. To prevent carbonation and maintenance of relative humidity, all specimens were stored in the vacuum up to the time of when the test started.

The analyses were performed at the Institute of Chemistry of São Carlos, University of São Paulo, using TGA 2050 Thermogravimetric Analyzer V5.1A equipment. The experimental conditions were: N₂ gas dynamic atmosphere (40 ml.min⁻¹); heating rate (10 °C.min⁻¹) and a platinum top-opened crucible. The samples were heated in the range of 20 to 900 °C at a constant rate. The Ca(OH)₂ was estimated from the weight loss measured in the TG curve between the initial and final temperature of the corresponding DTG peak.

Differential scanning calorimetry (DSC) was used to investigate the combined effect of silica fume and polymer on heat development in the pastes. A DSC 2010 Differential Scanning Calorimeter was

Table 1. The chemical composition of cement.

Chemical composition	CPV-ARI-Plus (%)
Loss on ignition	3.10
SiO ₂	18.99
Al ₂ O ₃	4.32
Fe ₂ O ₃	3.00
CaO total	64.7
MgO	0.68
SO ₃	3.01
Na ₂ O	0.03
K ₂ O :	0.85
CO ₂ :	1.81
RI	0.26
CaO	1.63

Table 2. Physical properties of cement.

Setting time (min)	Blaine surface area m ² /kg	Compressive strength (MPa) NBR 7215				
		1 day	3 days	7 days	28 days	
Initial	Final					
150.78	226.25	467.9	27.87	43.57	48.69	56.16

Table 3. The chemical compositions of silica fume.

Chemical composition	%
SiO ₂	94.3
Al ₂ O ₃	0.09
Fe ₂ O ₃	0.10
CaO	0.30
MgO	0.43
SO ₃	-
K ₂ O	0.83
Na ₂ O	0.27

used. The experimental conditions were: N₂ gas dynamic atmosphere (40 ml.min⁻¹); heating rate (10 °C.min⁻¹) and platinum top-opened crucible. The samples were heated in the range of 25 °C to 500 °C at a constant rate.

XRD was used to identify the polycrystalline phases of cement and hardened cement paste. The qualitative XRD investigation was performed in a Carl Zeiss-Jena Universal Diffractometer, URD6 model at the Institute of Chemistry of São Carlos, University of São Paulo.

4. Results and Discussion

Table 4 shows the mixture proportions investigated. Figures 1 and 2 show the TG curves of pastes with silica fume content of 5% and 10% respectively (P5 and P6). It can be seen that TG curves for these pastes consist of four zones:

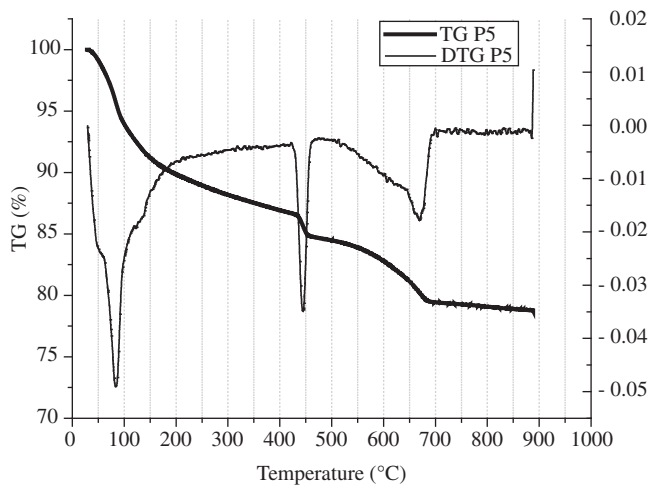
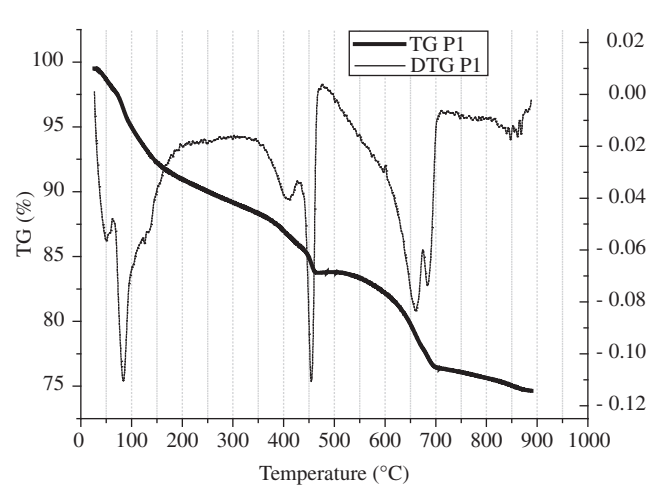
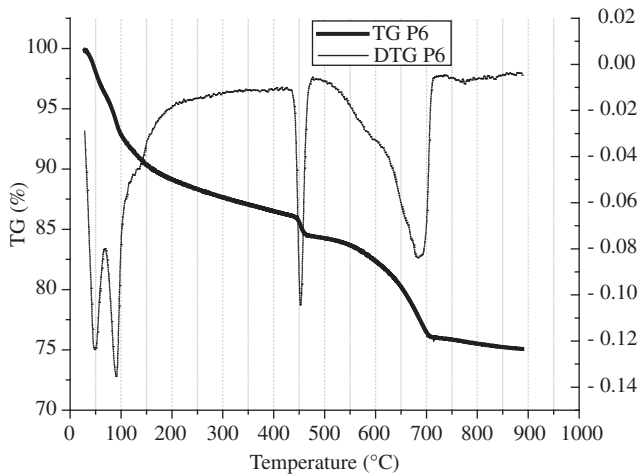
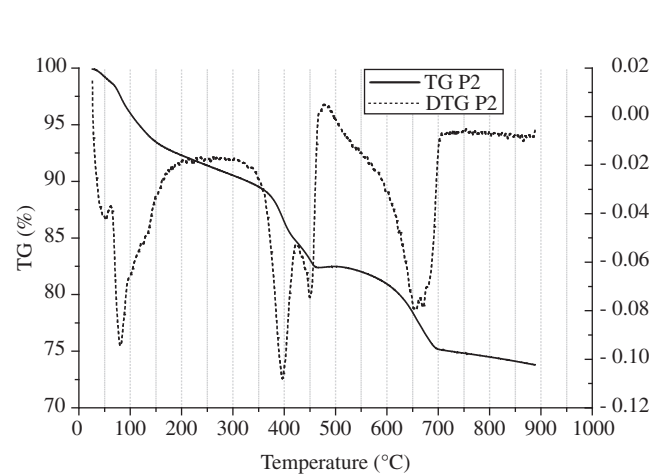
- ~ 25-123.3 °C: dehydration of pore water;
- ~ 123.3-420 °C: dehydration of calcium silicate hydrates;
- ~ 420-480 °C: dehydroxylation of calcium hydroxide; and
- ~ 480-730 °C: decarbonation of CaCO₃.

Figures 3 and 4 show the TG curves of pastes with 5% silica fume and polymer addition of 5.2% and 10.4% (polymeric solids), respectively. Figures 5 and 6 present TG curves of pastes with 10%

Table 4. Mixture proportion of the mortars.

Designation of paste	Silica fume content (%) [*]	Polymer Latex content (%) [*]	Solids of polymer content (%) [*]	Water/cement ratio
P1	5	10	5.2	0.36
P2	5	20	10.4	0.31
P3	10	10	5.2	0.36
P4	10	20	10.4	0.31
P5	5	0	0	0.36
P6	10	0	0	0.36

^{*}by weight of cement.

**Figure 1.** TG curve of the paste without polymer and 5% of silica fume P5.**Figure 3.** TG curve of the paste P1.**Figure 2.** TG curve of the paste without polymer and 10% of silica fume P6.**Figure 4.** TG curve of the paste P2.

silica fume and polymer addition of 5.2% and 10.4% (polymeric solids), respectively. The TG curves obtained in these tests are typical of hydrated cement pastes containing carbonate phases and polymeric admixtures. The curves can be divided into five major parts, according to different reactions:

- ~ 25-123.3 °C: dehydration of pore water;
- ~ 123.3-345 °C: dehydration of calcium silicate hydrates;
- ~ 345-427 °C: weight loss due to polymer pyrolysis and dehydration of part of silicate hydrates;

- ~ 427-475 °C: dehydroxylation of calcium hydroxide; and
- ~ 475-711 °C: decarbonation of CaCO_3 .

The weight loss for each temperature range can be seen in Table 5. Regarding pastes with polymer addition, the weight loss related to the dehydroxylation of calcium hydroxide is lower than pastes with silica fume addition alone.

Figure 7 shows the DSC curves obtained for the pastes studied. From these results it is clear that pastes with polymer present different results from the pastes which do not contain polymer. All curves

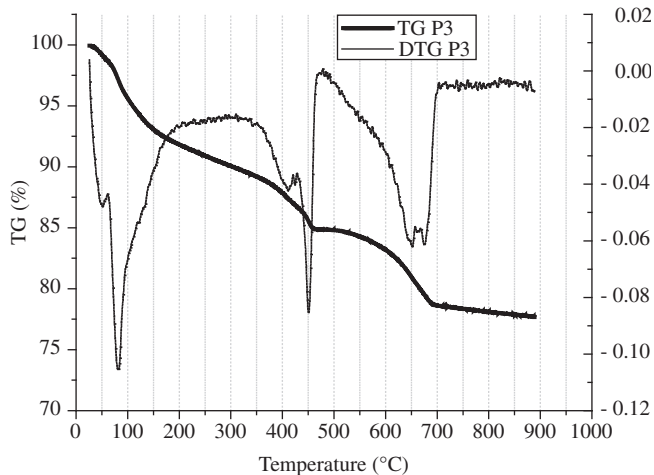


Figure 5. TG curve of the paste P3.

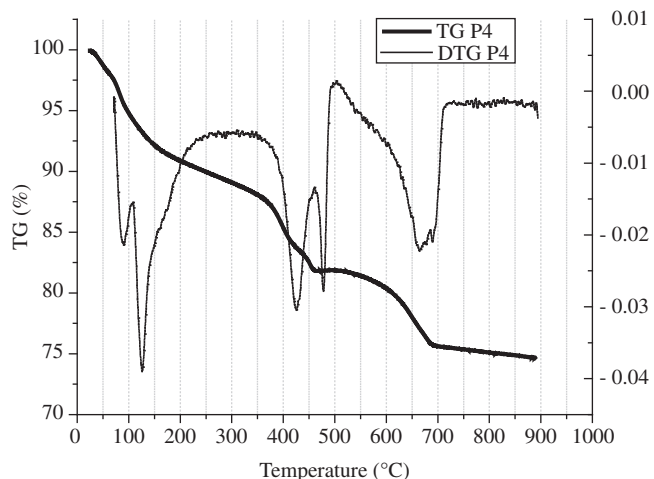


Figure 6. TG curve of the paste P4.

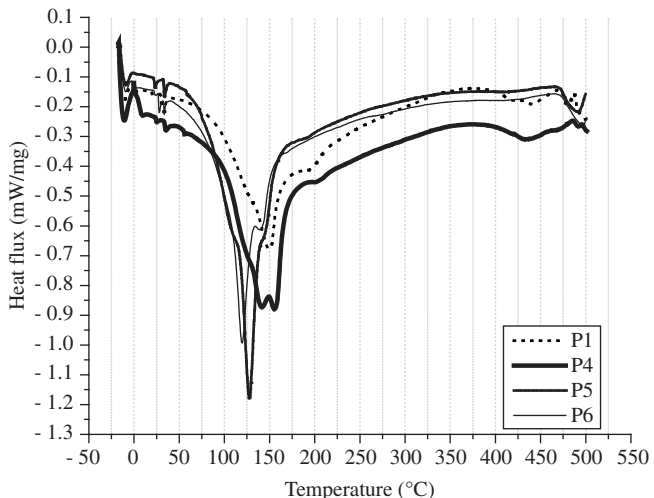


Figure 7. DSC curves of the pastes P1, P4, P5 and P6.

Table 5. Weight loss of the pastes according to the temperature.

	Temperature range (°C)	Weight loss (%)
P5	28.3 a 123.3	7.487
	123.3 a 416.2	5.75
	416.7 a 472.1	2.056
	472.1 a 702.3	5.258
	Residue above 850 °C	78.9
P6	25.2 a 123.3	8.43
	123.3 a 420.6	5.238
	420.6 a 478.8	1.876
	478.8 a 729.2	8.436
	Residue above 850 °C	75.23
P1	25.9 a 123.3	5.922
	123.3 a 337.9	5.037
	337.9 a 429.6	2.665
	429.6 a 481	2.095
	481 a 711.3	7.412
Residue above 850 °C	75.04	
P2	26.1 a 123.3	5.236
	123.3 a 333.4	4.767
	333.4 a 422.9	5.175
	422.9 a 478.8	2.301
	478.8 a 713.5	7.357
Residue above 850 °C	74.12	
P3	25.2 a 123.3	5.695
	123.3 a 344.6	4.949
	344.6 a 427.3	2.53
	427.3 a 474.3	1.912
	474.3 a 711.3	6.308
Residue above 850 °C	77.89	
P4	24.6 a 123.3	6.544
	123.3 a 344.6	5.175
	344.6 a 429.6	4.663
	429.6 a 476.5	1.707
	476.5 a 713.5	6.289
Residue above 850 °C	74.88	

show an endothermic peak around 480 °C, but they are more intense for pastes with silica fume alone because of the higher Ca(OH)₂ content. Pastes with silica fume and polymer present an exothermic peak around 350 °C, indicating polymer pyrolysis, as was found from the TG/DTG analyses. The pastes modified with polymer presented higher heat absorption between 100 °C and 200 °C, suggesting that these pastes contain more free water resulting from the hydration being delayed, and that these have a higher amount of calcium silicate hydrates.

The XRD results show some qualitative differences in the hydration rate due to the incorporation of silica and polymer. Figures 8, 9 and 10 show the X ray patterns of the pastes with 5%, 10% of silica fume, and pastes with polymer. The main compounds observed are Ca(OH)₂ in the form of portlandite, a small amount of CaCO₃ resulting from carbonation of Ca(OH)₂ which occurred during hydration and anhydrous calcium silicate. The peak intensity in the region of 2θ = 18° has been considered as a measurement of the intensity of Ca(OH)₂ for the comparison between the samples¹⁹. Therefore,

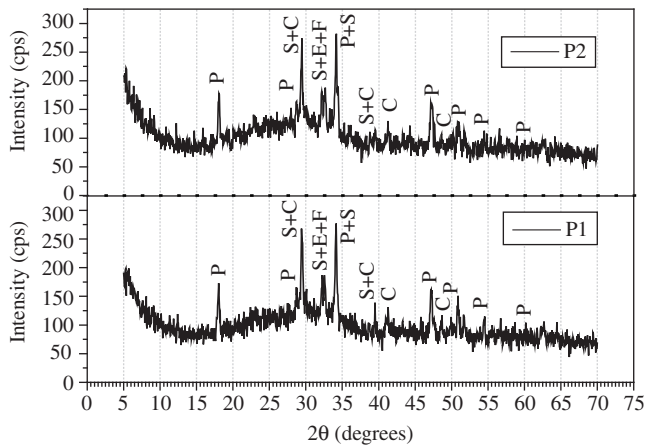


Figure 8. XRD patterns of the P1 and P2 pastes after 28 days of hydration. P. portlandite ($\text{Ca}(\text{OH})_2$); CC. Calcium carbonate (CaCO_3); E. ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$); S. silicates; F. ferrite.

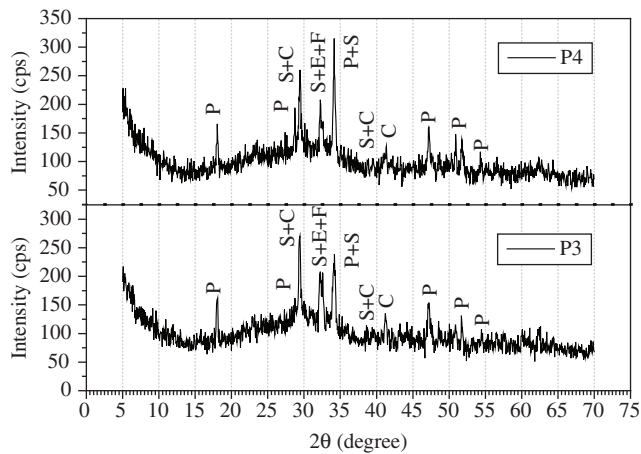


Figure 9. XRD patterns of the P3 and P4 pastes after 28 days of hydration. P. portlandite ($\text{Ca}(\text{OH})_2$); CC. Calcium carbonate (CaCO_3); E. ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$); S. silicates; F. ferrite.

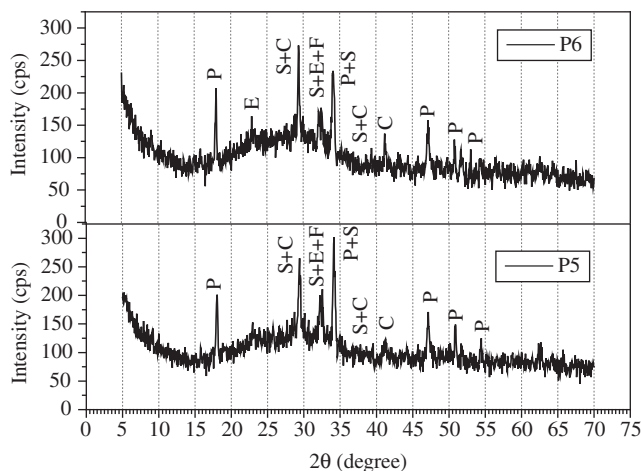


Figure 10. XRD patterns of the P5 and P6 pastes after 28 days of hydration. P. portlandite ($\text{Ca}(\text{OH})_2$); CC. Calcium carbonate (CaCO_3); E. ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$); S. silicates; F. ferrite.

Figures 8, 9 and 10 show that 10% of silica fume replacement and polymer addition resulted in the lowest peak intensity for the portlandite ($\text{Ca}(\text{OH})_2$).

5. Conclusions

The qualitative XRD investigation revealed that a lower intensity of $\text{Ca}(\text{OH})_2$ (in the region of $2\theta = 18^\circ$) was obtained in the presence of latex, compared to pastes without polymer. Similarly, we found a decrease in the $\text{Ca}(\text{OH})_2$ content in the TG analyses for pastes with polymer addition. As can be seen, pastes with polymer and 10% silica fume content presented the lowest $\text{Ca}(\text{OH})_2$ compared to the other pastes. From the thermogravimetric investigations performed, shown in the TG and DSC curves, it can be concluded that mineral admixtures and polymeric additions have influenced cement hydration, mainly when added simultaneously.

It can be concluded from the data reported in this paper and within the limits of the experimental conditions adopted that the additions studied resulted in the decrease of the portlandite content. Both the pozzolanic reaction, that transforms the weak calcium hydroxide crystals into the strong calcium silicate hydrate gel, and the delay of hydration due to polymer addition appear to cause a decrease in the portlandite content, contributing to the improvement of the mortars' performance studied earlier by the authors.

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