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Thermoanalytical and infrared spectroscopy investigations of some mineral pastes containing organic polymers

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Abstract

The interaction in the presence of water between organic polymers [two polyvinyl alcohol acetate (PVA1 and PVA2)-, one polyvinyl acetate (PVAc)-, and one acryloethyl–metacrylomethyl (R)-type copolymers] and inorganic materials ($3CaO{\cdot}Al_2O_3$+$CaSO_4{\cdot}2H_2O$, $12CaO{\cdot}7Al_2O_3$, and $CaO{\cdot}Al_2O_3$) was investigated using complex thermal analyses and infrared (IR) spectroscopy. The DTA curves of the 1-to 28-day-hydrated organo-mineral composite samples showed some significant differences in comparison with those of the hydrated inorganic materials. The most important differences consist in the presence of some exothermic peaks that are not attributable to the pure organic polymers. More than that, none of the specific effects of the pure organic polymers are evidenced on the DTA curves of the hydrated organo-mineral composite materials. This, in connection with their IR spectra, which clearly evidence the disappearance of some investigated polymers specific IR bands, can be considered as an indirect evidence of the cross-linking of polymer chains via metal ions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium aluminates; Polymers; Hydration

1. Introduction

Complex organic–inorganic binding compositions are the main components of MDF (macro-defect-free)-type masses. The presence of the organic polymer contributes, by its physical and chemical implication in the processes that determine the hardening of this kind of masses, to the development of performance properties concerning the flexural strength, callousness, and toughness [1]. The nature of the mineral binder, as well as the nature and amount of the organic polymer have a decisive influence on the behavior of this kind of composites, through the reactions they are involved in the presence of water.

Aluminous compounds like $3CaO{\cdot}Al_2O_3$ (C_3A), $12CaO{\cdot}7Al_2O_3$ ($C_{12}A_7$), and $CaO{\cdot}Al_2O_3$ (CA) have a high hydration rate and therefore are important for the hydration and hardening of Portland and aluminous cement, as well as for complex organic–inorganic binding materials, based on such cements.

Information concerning the reaction processes in calcium aluminate–polymer–water systems [2–7] permit to outline the following ideas concerning the implication of the polymer in these processes:

- the presence of polymers changes the kinetics of the inorganic material–water reaction processes, as well as the structure development of the hydrated compounds;
- depending on their nature, the polymers participate in the reaction processes in the complex systems; therefore are formed, beside calcium aluminate hydrates, some organic–inorganic compounds of high complexity.

In this paper are revealed thermal analyses and infrared (IR) spectroscopy information regarding the reaction processes at the hardening of C_3A–$CaSO_4{\cdot}2H_2O$–H_2O, $C_{12}A_7$–H_2O, and CA–H_2O in the presence of some organic polymers—polyvinyl alcohol acetate (PVA1 and PVA2),

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Table 1
Mix proportions (wt.%) of the investigated compositions

	Calcium aluminates			Polymers			
Sample symbol	C_3A+CsH_2[a]	$C_{12}A_7$	CA	PVA1	PVA2	PVAc	R
A0	100	–	–	–	–	–	–
A3	85	–	–	–	–	–	15
A7	85	–	–	–	15	–	–
B0	–	100	–	–	–	–	–
B1	–	80	–	20	–	–	–
B2	–	80	–	–	20	–	–
B3	–	80	–	–	–	20	–
C0	–	–	100	–	–	–	–
C1	–	–	80	20	–	–	–
C2	–	–	80	–	20	–	–
C3	–	–	80	–	–	20	–

[a] The molar ratio C_3A/CsH_2 was 4:3.

polyvinyl acetate (PVAc), and acryloethyl–metacrylomethyl (R) copolymer.

2. Experimental

The calcium aluminates—C_3A, $C_{12}A_7$, and CA—were obtained by heating unto complete CaO assimilation of stoichiometric mixes made from chemical-grade $CaCO_3$ and Al_2O_3, followed by the fine grinding of the sintered compounds. Chemical-grade $CaSO_4{\cdot}2H_2O$ (CsH_2) and the following polymers were used:

- PVA1 and PVA2, having an average polymerization degree of about 500 and 900, respectively, and a degree of hydrolysis of 88% and 98%, respectively;
- PVAc;
- R copolymer.

Taking into account our previously obtained information [6,7] concerning the binding behavior of calcium aluminate–water systems containing up to 20 wt.% of the above-mentioned polymers, the present paper used thermal analyses and IR spectroscopy and the compositions are shown in Table 1. Pastes were prepared from these compositions (using a water/solid ratio 0.60 for A masses and 0.65 for B and C masses) and hydrated in closed bottles until 28 days. Prior to their examination by IR and DTA, the hydration processes were stopped by rinsing with acetone and drying at 50–60 °C.

3. Results and discussion

3.1. The $3CaO{\cdot}Al_2O_3$–$CaSO_4{\cdot}2H_2O$–polymer–H_2O system

The thermal analyses corroborated with X-ray diffraction analyses evidenced a retarding effect of the polymers on the reaction C_3A+$CaSO_4{\cdot}2H_2O$+H_2O, which becomes more pronounced with the addition of R-type polymer. The presence of the polymers retards the ettringite→monosulphate transformation, probable due to their adsorption on the ettringite particles.

The DTA curves of the C_3A+CsH_2+H samples containing PVA2 and R evidence important differences as compared with the samples without polymers (see Fig. 1).

The DTA of the 1-day-hydrated A0 sample shows a single strong endothermic peak at 153 °C, corresponding to

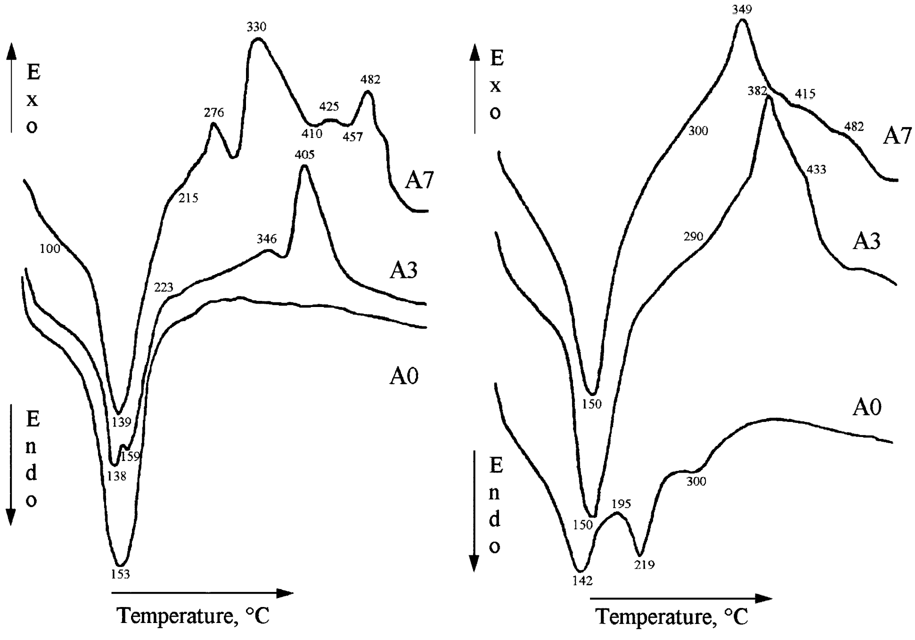

Fig. 1. DTA of A0, A3, and A7 samples, after 1- (left) and 28-day (right) hydration time.

the dehydration of AFt phases (evidenced by X-ray analyses) and of unreacted gypsum. After a 28-day hydration time, the endotherms on the DTA clearly evidence the effects corresponding to the dehydration in two steps of ettringite (142 and 219 °C) and monosulphate (219 and 300 °C). The transformation of ettringite in monosulphate was also supported by X-ray analyses.

The DTA curves of the A7 sample containing PVA2 evidence two kinds of effects:

- one large endothermic peak at 139–150 °C caused by the dehydration of calcium sulphate-containing compounds (ettringite, gypsum, and monosulphate);
- some well-shaped exothermic peaks, especially after 1 day of hydration, at 276, 330, 425, and 482 °C, attributable to the burning of the organic compound.

As compared to the DTA of the pure PVA2 (Fig. 2), the exotherms at the hydrated A7 sample are smaller and occur at somewhat different temperatures, especially after later hydration terms. Thus, after 28-day hydration time, only one well-shaped exothermic peak at 349 °C is visible.

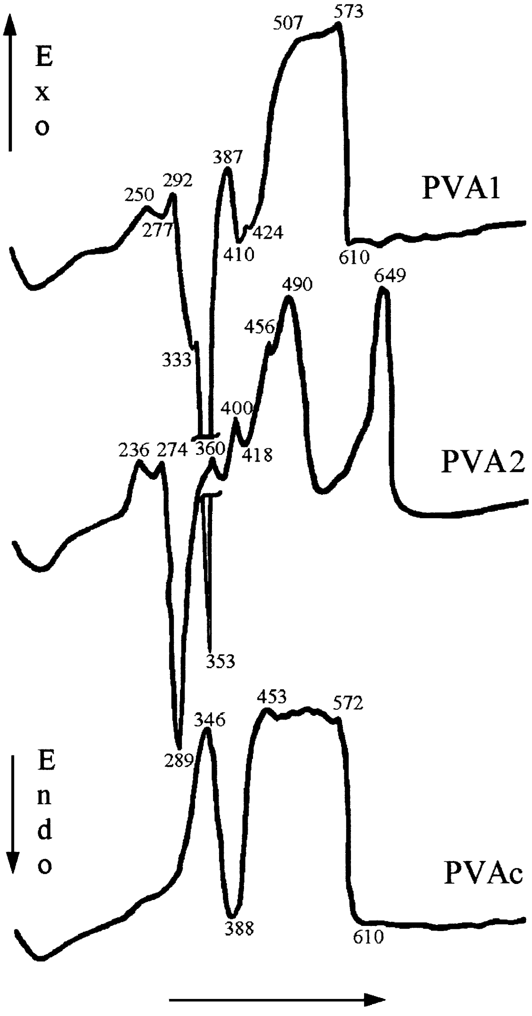

Fig. 2. DTA of the PVA1, PVA2, and PVAc.

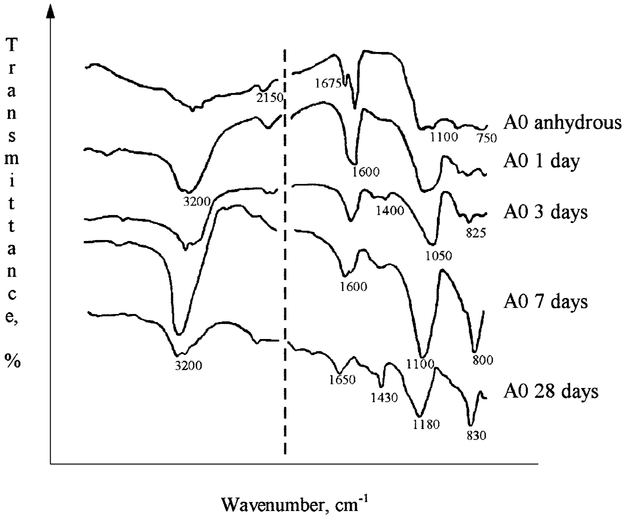

Fig. 3. IR spectra of composition A0—anhydrous and after 1-, 3-, 7-, and 28-day hydration time.

The DTA of the A3 sample containing R-type copolymer evidences after 1-day hydration of endotherms at low temperatures (138 and 159 °C), which resemble best the dehydration curves of gypsum. These suggest a stronger retarding effect of R on the reaction processes, which is also corroborated by X-ray analyses. The exotherms attributable to the polymer burning are well shaped on the DTA of the 1-day-hydrated A3 sample (346 and 405 °C). After a 28-day hydration time, they appear at different temperatures and with a changed shape, which may suggest the formation of organic–inorganic compounds.

The decrease of the amplitude and number of the exotherms specific to the polymers may be considered as an indirect indication of their participation in chemical reactions in the $C_3A–CsH_2–H$–polymer system, which progresses in time.

The IR spectroscopy analyses provide supplementary information concerning the polymers' participation in the reaction processes. Figs. 3–5 present the IR spectra of the A0, A3, and A7 samples—anhydrous and after 1- to 28-day hydration time.

The IR spectra of the A0 sample (Fig. 3) evidence even after the first day of hydration, with the characteristic absorption bands of ettringite at 1050–1100, 1600, and 3200 cm^{-1} [8]. The amplitude of these bands increases in time, but after 7-day hydration, when the ettringite (AFt)$\rightarrow$monosulphate (AFm) transformation starts, they diminish (AFm contains less sulphate and water than AFt), except the band at 800–830 cm^{-1}, which is specific to Al–O bonds.

The presence of PVA2 in the anhydrous sample A7 (Fig. 4) is evidenced by the absorption bands at 800–925, 1100, 1450, 1675, 2750, and 3150 cm^{-1} [9]. On the IR spectra of the hydrated A7 samples, the amplitude of these

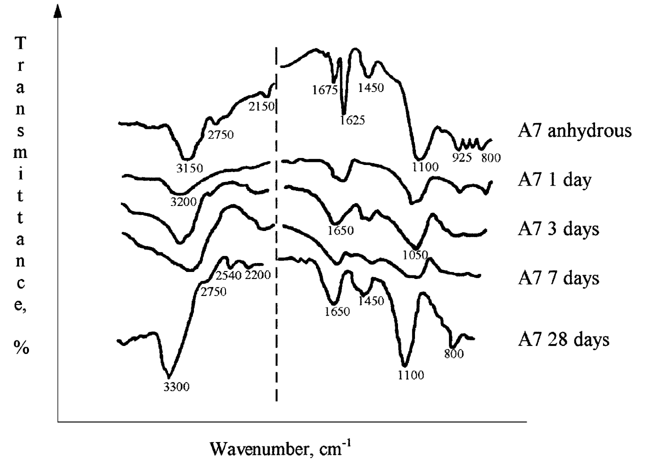

Fig. 4. IR spectra of composition A7—anhydrous and after 1-, 3-, 7-, and 28-day hydration time.

bands diminishes progressively close to disappearance and this is associated with the appearance of a new band at 2540 cm^{-1} clearly evidenced on the IR spectra of the 28-day-hydrated A7 sample.

These modifications in the IR spectra may be considered as indications of the role of the polymer in the chemical reactions that occur in the system (which may be due to the formation of a chelatic compound). The retarding effect of PVA2 on the formation of hydrated compounds and their conversion is shown by the fact that after the 28-day hydration time of A7, the amplitudes of the ettringite bands are comparable to those with 7-day hydration time in the A0 sample (without polymer).

The IR spectra of the samples containing 15 wt.% R (Fig. 5), hydrated for 1 and 3 days, show a band at 1725 cm^{-1}—specific to the CO bond of the acrylic polymer [10]. After longer hydration terms, the amplitude of this band decreases near to disappearance. These suggest the existence of some reaction processes between the acrylic copolymer and the mineral binder. The large absorption band that appears at 1650 cm^{-1} may overlap a band at 1550 cm^{-1} specific to some newly formed Me–COO links in the organic–inorganic reaction compounds [10].

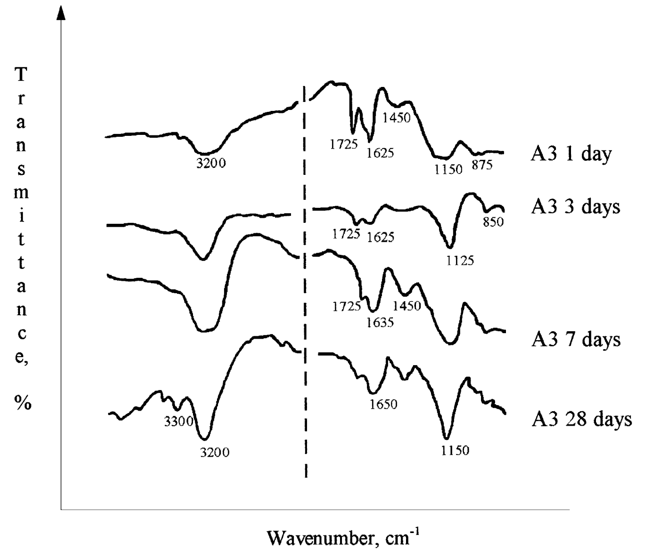

Fig. 5. IR spectra of composition A3 after 1-, 3-, 7-, and 28-day hydration time.

3.2. The $C_{12}A_7$–polymer–H_2O system

The DTA curves of the 1-day-hydrated $C_{12}A_7$–polymer compositions (B0–B3) are shown in Fig. 6. The endotherms at 162 and 266 °C visible on the DTA of sample B0 can be attributed to the dehydration of C_2AH_8 and $Al(OH)_3$. The DTA curves of the 20 wt.% polymer (PVA1, PVA2, or PVAc)-containing compositions show a third endothermic peak at low temperatures (108–128 °C), which can be attributed to the dehydration of CAH_{10}, also emphasized by X-ray diffraction analysis. These suggest that the presence of the polymers used in our research favors the formation of CAH_{10}, besides C_2AH_8.

The specific thermal peaks of the polymers (see Fig. 2) appear in Fig. 6 at modified temperatures and with changed shapes. The number of the peaks specific to the organic compounds, as well as their characteristic temperatures

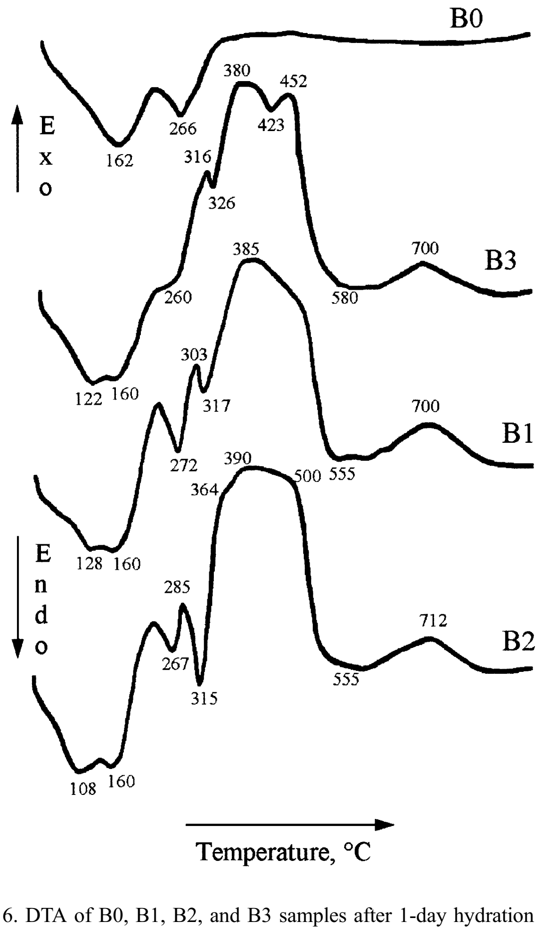

Fig. 6. DTA of B0, B1, B2, and B3 samples after 1-day hydration time.

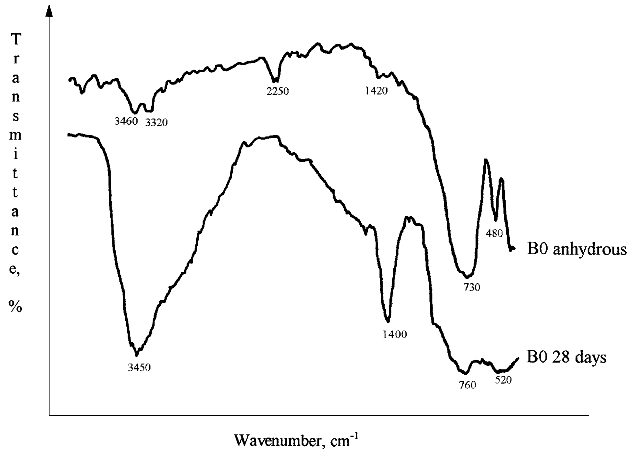

Fig. 7. IR spectra of composition B0—anhydrous and after 28-day hydration time.

diminish. From the multiple peaks specific to PVA1 and PVA2, only one large exothermic peak located between 315 and 555 °C appeared on the DTA curves of the hydrated binders. The three exotherms specific to PVAc are evidenced on the DTA of the hydrated B3 with modified shape and at 50–100 °C lower temperatures as compared to PVAc effects. An essential difference that appears on the curves in Fig. 6 is the presence of a large exothermic peak at 700–712 °C, which neither occur on the polymers' DTA nor on those of the hydrated B0 sample. This peak is associated with a weight loss of about 4.5–5% and may suggest the formation of some organic–mineral compounds, which stable on such high temperatures.

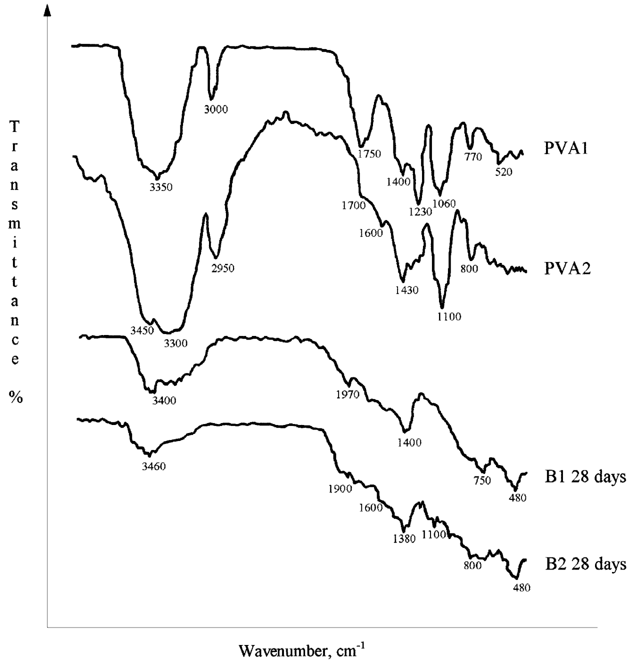

Fig. 8. IR spectra of PVA1 and PVA2 and 28-day hydrated B1 and B2 samples.

The IR spectra presented in Figs. 7 and 8 sustain the information obtained by DTA concerning the existence of mineral binder–polymer–water-type reaction processes. This is evidenced by the comparison of the IR spectra of 28-day hydrated mixed binder compositions (see Fig. 8, B1: 28 days, B2: 28 days) to those of polymers (see Fig. 8, PVA1 and PVA2) and that of the polymer-free $C_{12}A_7$ at the same hydration term (see Fig. 7, B0: 28 days).

The IR spectrum of the $C_{12}A_7$+H_2O (B0) sample shows a large absorption band at 3450 cm^{-1} and another at 1400 cm^{-1}, corresponding to molecular and hydroxyl water, as well as to $CaCO_3$, which inevitably forms. Besides these, small absorption bands appear at 760 cm^{-1}, specific to $[AlO_4]$ groups, and at 520 cm^{-1}, specific to $[AlO_6]$ groups.

The IR spectrum of the B1 sample hydrated for 28 days shows the absence of the specific bands of PVA1—3000, 1750, 1230, and 1060 cm^{-1}—as well as some transformations appreciated by shifts of the bands towards lower frequencies (770→750 cm^{-1}; 520→480 cm^{-1}) and even the appearance of a new vibration band at 1970 cm^{-1} (probably due to various types of −COOH substitutions).

The disappearance of the band at 1700 cm^{-1} (the degree of hydrolysis is 98% as compared with PVA1), the shift of the band at 1430 cm^{-1} (δOH and δOH_2^-) towards 1380 cm^{-1}, as well as the appearance of a new band at 1900 cm^{-1}, are

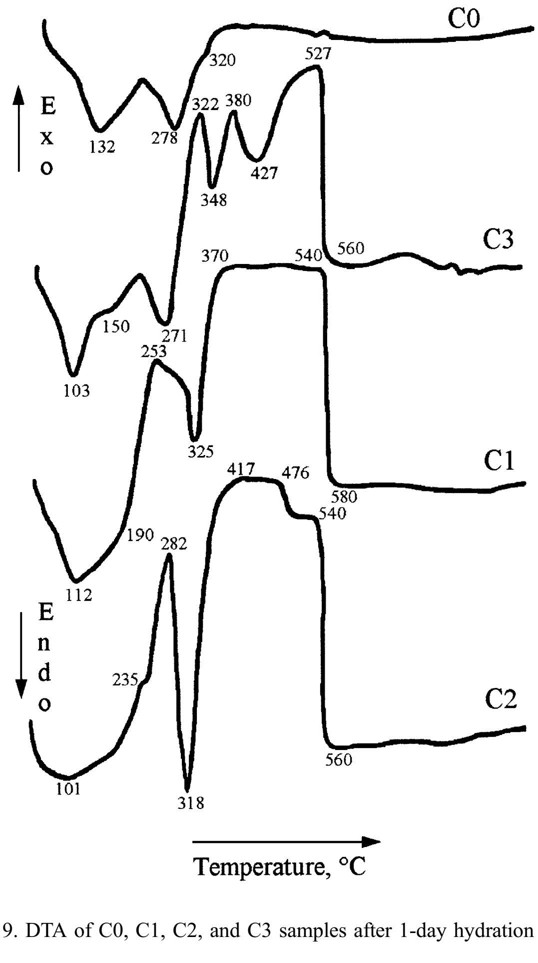

Fig. 9. DTA of C0, C1, C2, and C3 samples after 1-day hydration time.

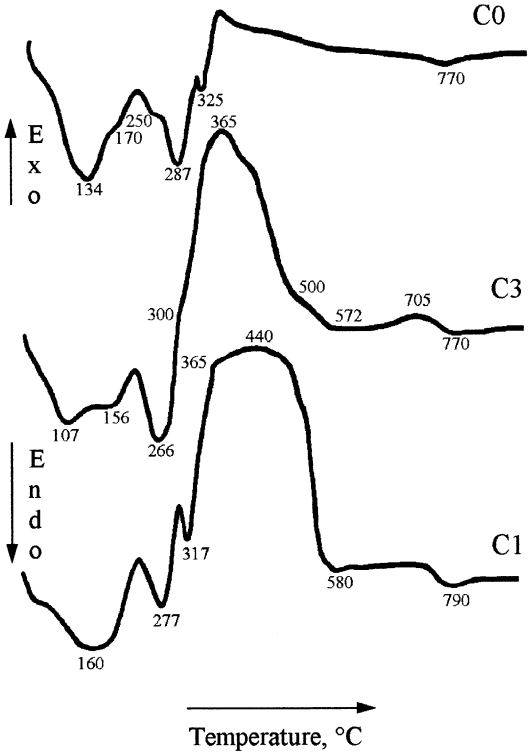

Fig. 10. DTA of C0, C1, and C3 samples after 28-day hydration time.

important modifications that occur on the IR spectrum of the B2 sample hydrated for 28 days.

All these observations clearly suggest the implication of the used polymers in interaction processes with the mineral binding matrix.

3.3. The CA–polymer–H_2O system

The comparison of the DTA curves of the polymers (shown in Fig. 2) with those of the CA–polymer samples hydrated for 1 and 28 days (Figs. 9 and 10) provides information concerning possible polymer–mineral compound reaction processes, but does not allow any specification about the nature of the newly formed compounds.

At the hydration of CA with 20 wt.% polyvinyl alcohol, the intensity of the pronounced endotherms at 289 and 353 °C is diminished, especially for the PVA1-containing sample, and the temperatures are changed as compared to those specific to the polymers. These modifications are stronger at longer hydration terms (see Figs. 2, 9, and 10 for the peaks at 353, 325, and 317 °C). The large exothermic peak between 424 and 610 °C, with a maximum at 507–573 °C and specific to PVA1, shifted to lower temperatures when the hydration time is longer.

At the hydration of CA with 20 wt.% PVA2, the five distinct exotherms at 360, 400, 456, 490, and 649 °C, evidenced on the DTA of the pure polymer (see Fig. 2), are merged in a single large exothermic peak with maxim between 417 and 540 °C.

At the hydration of CA with 20 wt.% PVAc, the two DTA peaks of the polymer (at 346 and 453–572 °C as seen in Fig. 2) divide after 1-day hydration in three distinct exotherms at 322, 380, and 527 °C and merge into one large exothermic peak at 365 °C after a 28-day hydration time.

The somewhat similar shape of the exotherms for the 28-day hydrated CA+20 wt.% polymer samples may suggest that the same kinds of organic–mineral compounds are formed, unaffected by the nature of the used polymer, because in the basic system the PVAc is hydrolyzed and transformed into PVA.

4. Conclusions

1. Thermoanalytical and IR spectroscopy investigations are very suitable techniques to analyse the interaction processes between mineral pastes (C3A+CsH2, C12A7, and CA) and organic polymers (PVA1, PVA2, PVAc, and R).
2. All the used polymers retard the hydration of mineral pastes; the copolymer R has a stronger retarding effect as compared to the alcohols and their derivative compound.
3. In the presence of polymers, same mineral hydrates are formed. They show a lower degree of crystallinity and are present in smaller proportions as compared to the polymer-free samples. The AFt→AFm conversion is retarded. CAH10 formation is favored.
4. Besides the mineral hydrates, by cross-linking of polymer chains via metal ions organo-mineral compounds are formed. Their structure changed in time during the hydration processes.

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