

THERMAL EVIDENCES OF THE INTERACTION BETWEEN PLASTICIZERS AND Ca SALTS IN CEMENT

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The interactions between an organic polymer with plasticizing activity and a model surface (CaCO_3), with a surface activity similar to the cement one, have been analysed by volumetric analysis and thermal analysis: TG/DTG and DSC. The synthesized polymer has a negative link site (carboxylate) that is able to interact with the substrate and a long ethylene oxide chain that contribute to the dispersing activity. The pattern of the adsorption isotherm suggests the occurring of a step like adsorption, initially characterised by a coil conformation of PEO chain followed by a more PEO strained, linear, conformation as the amount of polymer increases. The polymer adsorption appears to modify the crystalline phase and morphology of the CaCO_3 surface as the thermal analysis puts in evidence through the CaCO_3 decomposition temperature shifts. SEM analysis confirms the morphology changes induced by polymer adsorption.

Keywords: Ca salts, cement plasticizer, polymer adsorption

Introduction

Superplasticizers (SP) improve fluidity by dispersing cement particles in a paste: they allow the working of the fresh materials by reducing the water quantity [1], and, as a result, they greatly enhance the material durability by reducing the porosity of hardened concrete.

We are engaged in the study of the complex interaction between cement and a class of polymer dispersant.

The understanding of the cement-superplasticizer interaction indeed is quite complicated due to the hydration reactions of cement that is a reactive multi-mineral mixture with surface properties continuously evolving [2]. In order to analyse the adsorption of the polymer and cement, we used a single component powder as a model substrate of the cement [1–5]. Our aim was to analyse only the salt formation between the anionic function of the SP and alkaline ions in the Stern layer excluding all the other chemical surface phenomena. The powder simulates the polymer's interaction with cement at the beginning of the hydration reaction (time zero $t \sim 0$). Calcium salts (CaCO_3) present some tailored characteristics to simulate the cement at the zero time of hydration reaction in presence of dispersant carboxylate type polymer [6].

We studied a polymer (PEO-SA) whose structure may be considered the fundamental unit of carboxylate superplasticizer (PC). PEO-SA have a negative link site (carboxylic acid) that is able to interact with the substrate and a long ethylene chain

(MPEG M_w 1000) that is supposed to contribute to the dispersing activity. The free carboxyl group of the linear polymer (PEO-SA) is supposed to absorb on the carbonate surface forming Ca salts like over the cement powder. The polymer is known to have a dispersant activity in colloidal suspension [7] and we observed the same activity in cement paste. In future we will investigate deeply this behaviour.

By using PEO-SA polymer we mean to simplify the scenario of the complex adsorption mechanism, so to evaluate the role of the link site and the dispersant chain only.

The aim of this study is to characterise the behaviour of PC superplasticizers and to have some inputs to design new structures. The interaction polymer CaCO_3 has been studied with TG/DTG analysis, titration and scanning electron microscopy (SEM).

Experimental

Materials

PEO-SA polymer was synthesized by selective esterification following the scheme of Fig. 1. Succinic anhydride, and pyridine were purchased from Aldrich Chem. Co., and used as received.

Mono-methoxy terminated polyethyleneglycol (MPEG; M_w 1000 g mol^{-1}), from Aldrich, was dried by azeotropic distillation with toluene before the use.

MPEG (0.05 mol) was dissolved in chloroform (200 mL). Succinic anhydride (0.05 mol) and

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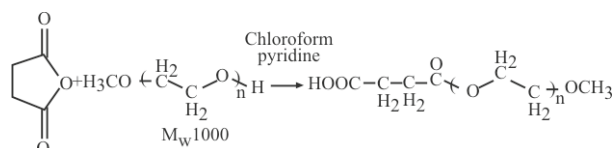


Fig. 1 Synthesis scheme of PEO-SA

pyridine (0.06 mol) were added to the chloroform solution, and the mixture was reacted at 60°C for 75 h [8]. The solution was cooled at room temperature and concentrated to dryness by rotary evaporation. The obtained wax was dissolved in water, acidified with a solution of HCl 1 M to pH 1 about. The water phase was washed with diethyl ether, extracted with chloroform, and dried with anhydrous sodium sulphate. The solution was filtered and concentrated to dryness.

^1H NMR (CDCl_3): 3.65 (s, OCH_2CH_2), 2.48 (t, CH_2).

The CaCO_3 (Table 1) was purchased from Fluka and characterized by X-ray diffraction analysis (Philips PW 1130) and particle size distribution analysis (measured by CILAS 1180 Liquid).

Table 1 Physical parameters of CaCO_3

Material	BET specific surface/ $\text{m}^2 \text{g}^{-1}$	Average particle size/ μm	Isoelectric point pH
CaCO_3	0.6	26.4	10

Methods

The test set-up is represented in the flow diagram reported in Fig. 2.

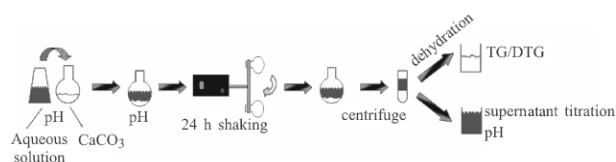


Fig. 2 Adsorption test set-up

Adsorption

Adsorption isotherms were obtained at room temperature (20°C).

Solutions with increasing concentrations of PEO-SA were prepared, according to Table 2. A constant aqueous solution/ CaCO_3 volume/mass ratio of 2 was used (60 mL of aqueous solution to 30 g of CaCO_3).

Deionised water in place of the aqueous polymer solution was used for the hydration of CaCO_3 blank test.

In addition the fluctuation of the pH value was monitored during the adsorption analysis. The initial pH suspension value and that at the equilibrium of the supernatant were evaluated.

Table 2 Analysis codes used to identify the aqueous solutions containing PEO-SA in different concentrations

Analysis code	polymer/ CaCO_3 ratio/ mg g^{-1}	Analysis code	polymer/ CaCO_3 ratio/ mg g^{-1}
A-005	3.5	A-010	11
A-006	4.5	A-011	13
A-007	6.0	A-012	16
A-008	7.0	A-013	20
A-009	9.0	A-014	24

The suspensions were then equilibrated for 24 h on a vertical shaker. The suspension was then centrifuged for 5 min. The supernatants were removed from the samples and analyzed by titration with $\text{NaOH } 1 \cdot 10^{-3} \text{ M}$. The adsorbed concentrations were obtained from the difference between the initial and equilibrium concentrations.

The CaCO_3 powder obtained after polymer adsorption was dried under vacuum (50°C; 5 h) and then studied with thermal analysis

Instruments

Simultaneous TG/DTG and mass analysis were performed using 'Seiko TG/DTA 6300' with linked Pfeiffer Vacuum TermostarTM instruments for the mass analysis under nitrogen flow (50 mL min^{-1}).

The DSC analyses were performed using 'Seiko DSC 6200' in a nitrogen flow (130 mL min^{-1}).

The crystalline modification induced by plasticizer on CaCO_3 was analyzed also with XRD analysis using a Philips PW 1130 with copper cathode while the morphology of the powder was analysed using a scanning electron microscopy (SEM) (StereoScan 430, equipped with a backscattered electron detector; Leica Cambridge Instruments, Cambridge, UK). All of the samples were coated with gold by the sputtering technique (Sputter Coater SC7640; Polaron, Hertfordshire, UK).

Thermal analysis

Samples in TG/DTG/DTA were heated from 20 to 900°C. Heating rate of 5°C min^{-1} from 20 to 400°C and $10^\circ\text{C min}^{-1}$ from 400 to 900°C were applied in order to evaluate the polymer mass loss.

The samples in DSC were cooled down to 0°C and then heated from 0 to 500°C. Heating rate was $20^\circ\text{C min}^{-1}$. The isotherm curves from DSC analysis were obtained by calculating the mass (mg) of adsorbed polymer from the fusion enthalpy peak (20°C) of the adsorbed polymer compared with that of the pure polymer. The amount of the adsorbed polymer obtained by DSC, is lower than that obtained by titration. This is probably due to the fact that the heat re-

leased from the sample during the test is irradiated at high temperature and the instrument measure refer only to the bottom of the sample.

Results and discussion

To evaluate the phase modifications induced by the plasticizer on CaCO_3 we analysed the powder obtained after the PEO-SA polymer adsorption, by XRD analysis. In Figs 3a and b XRD spectra respectively of pure CaCO_3 and CaCO_3 with PEO-SA adsorbed on it are reported. The line does not show any differences. In fact in both cases the XRD spectrum presents only the peaks of calcite, a crystalline phase of CaCO_3 . Since XRD analysis cannot be considered, in our opinion, as a sensible technique to mark the parameters of the interactions between CaCO_3 and the plasticizer.

Adsorption isotherm obtained by titration of supernatant solution is reported in Fig. 4. The line pattern can be interpreted by examining three segments that, as enhanced in Fig. 4, have different slopes:

- Polymer adsorption initially increases as the concentration of aqueous solution raises;

- Then an intermediate region occurs in which polymer adsorption stays constant in the range of $3.5\text{--}8\text{ mg g}^{-1}\text{ CaCO}_3$ (plateau).
- For high values of PEO-SA concentration in the aqueous solution, the polymer adsorption increases again.

Accordingly we assume that two different families exist at low and high polymer concentrations of aqueous solution. The isotherm curve reported in Fig. 5 obtained by DSC analysis present the same three-step line of the curve obtained by titration. The only difference between the two curves is the amount of adsorbed polymer: the DSC curves present a lower mass amount of PEO-SA adsorbed for g of CaCO_3 than the titration curve one. However one can confirm the three fragments distinguished in the isotherm curve and then it is worthy to assume the existence of two different types of adsorption at low and high polymer concentrations of aqueous solution.

A review of literature [7, 9, 10] suggests a step isotherm model adsorption which satisfactorily explains the observed behaviour: the model assumes a different polymer conformation as the concentration of the aqueous solution changes. There are two regimes: a ‘mushroom’ regime at low concentration and

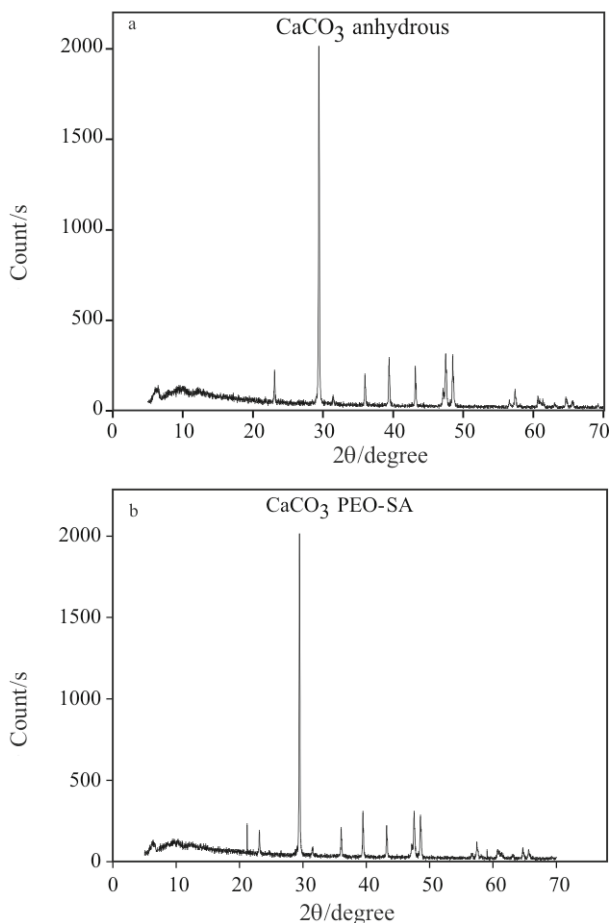


Fig. 3 XRD spectra

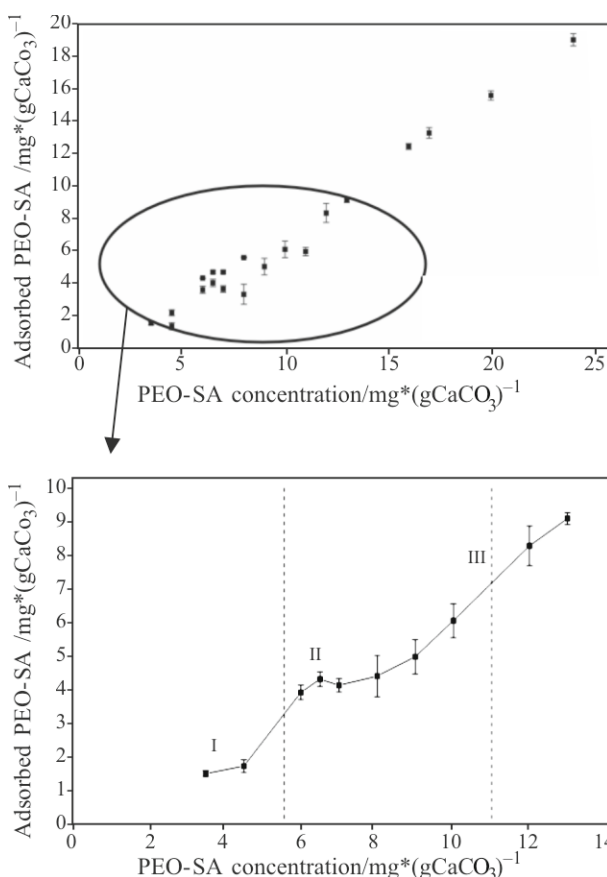


Fig. 4 Adsorption Isotherm of PEO-SA on CaCO_3 obtained by supernatant titration

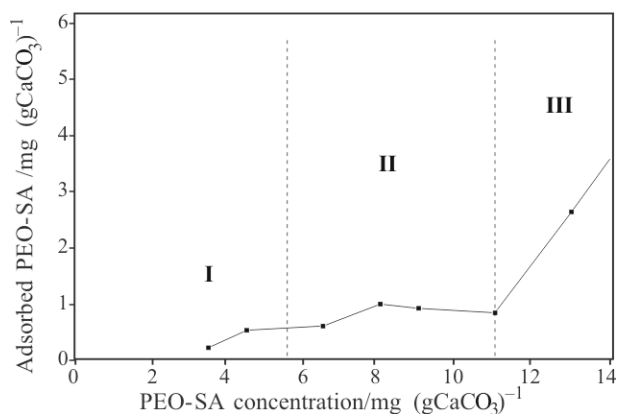


Fig. 5 Adsorption Isotherm of PEO-SA on CaCO_3 obtained by DSC analysis

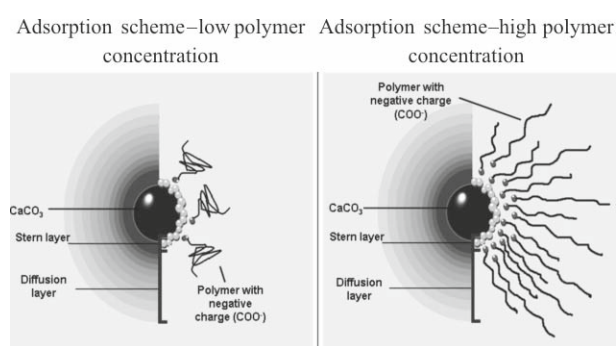


Fig. 6 Step isotherm model

a 'brush' regime at high concentration (Fig. 6). The first conformation occurs at low concentration of polymer solution; it allows only a limited coverage of the CaCO_3 surface and a coil distribution of MPEG chain. The second conformation is characterised by an increased order of the spatial distribution: high concentration of polymer, related to a rise of the grafting density, permits high surface coverage through the chain stretching.

Thermogravimetric analysis also shows two different families of curves. CaCO_3 TG/DTG and DSC decomposition patterns depend on the amount of adsorbed polymer. From the analysis of the graphs (Figs 7 and 8) it is possible to better discriminate between low and high concentration of polymer amount. The separation just occurs between the low concentration zone of the isotherm adsorption (before the plateau), and the high concentration region (after the plateau) (Fig. 4).

The TG curves reported in Fig. 7 show an increasing mass loss temperature for high polymer concentration. The same behaviour can be observed in the DTG curves (Fig. 8) where the decomposition of CaCO_3 , seems to be influenced by the occurring of the CaCO_3 /PEO-SA hybrid system.

In the range 550–817°C indeed the peak maximum of DTG curves shifts from the lower tempera-

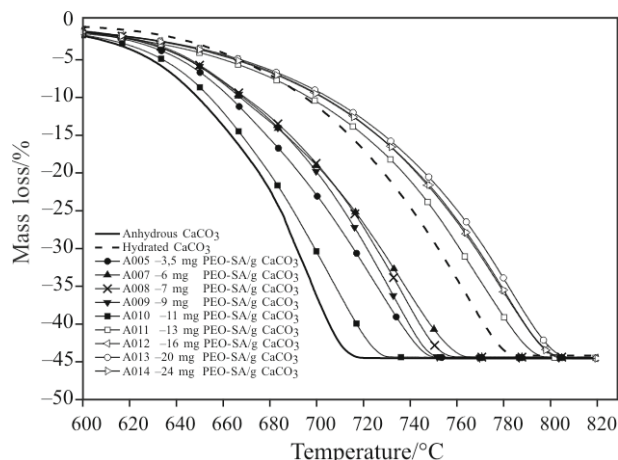


Fig. 7 TG curves of CaCO_3 and CaCO_3 /PEO-SA changing the amount of polymer used

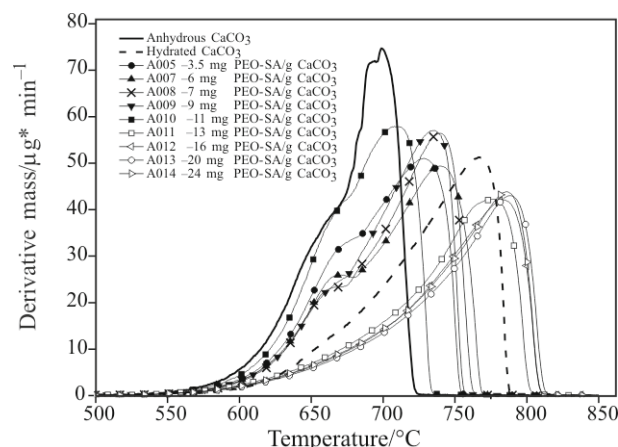


Fig. 8 DTG curves of CaCO_3 and CaCO_3 /PEO-SA at different amount of polymer used

ture, to higher values. The increase seems to relate to the PEO-SA adsorbed amounts. At adsorbed amounts higher than those of the plateau observed in the adsorption isotherm, the temperature is higher than the decomposition temperature of hydrated CaCO_3 . The observed phenomena can be attributed to morphological changes induced by the PEO-SA polymer

The DTG curve (Fig. 8) shows at low concentration (between anhydrous CaCO_3 and hydrated CaCO_3) two decomposition peaks: the first between 650–700°C is a shoulder of the major peak situated between 700–750°C. Following the literature [11, 12], the first peak may be attributed to the amorphous phase of CaCO_3 , the last one to the calcite phase of crystalline CaCO_3 .

The DTG curves at low concentration show a decreasing relevance of the first peak at increasing the amount of polymer towards near to the hydrated CaCO_3 decomposition signal. It is possible to hypothesize that the film of the adsorbed polymer which is in the coil conformation, opposes itself to the water per-

meation. At the high concentration the first peak of CaCO_3 decomposition disappeared and let us to suppose that the increasing percent of the stretch linear conformation, forms an organic cover more permeable to water than the first coil one.

Then the carboxylate polymer at high concentrations in the aqueous solution, seems to induce a surface modification on the amorphous phase of CaCO_3 which may be considered more soluble allowing the CaCO_3 form becoming more and more hydrated.

Other relate the influence of carboxylic acid on the crystalline phase of CaCO_3 [13, 14].

Scanning electron microscopy shows a surface modification of CaCO_3 (Fig. 9).

Anhydrous CaCO_3 and CaCO_3 present a typical surface of the inorganic crystal that is a square shaped surface as see in Fig. 9a.

The addition of a low concentration of polymer (Fig. 9b) does not modify the crystalline structure of calcium salts: there are not visible differences comparing Figs 9a and b.

Instead when the CaCO_3 powder adsorbs high concentration of carboxylate polymer the modification induced by the plasticizer is visible (Fig. 9c): the surface presents a complex pattern structure.

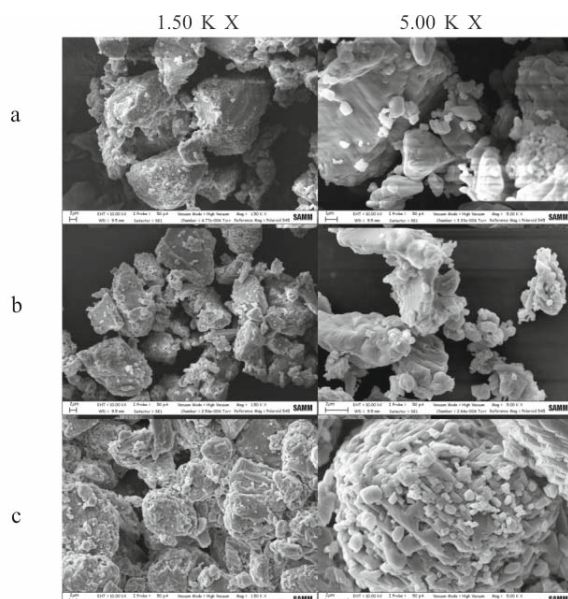


Fig. 9 Scanning electron microscopy of a – anhydrous CaCO_3 ; CaCO_3 /PEO-SA respectively at b – low concentration of polymer and c – at high concentration of polymer

Conclusions

According to literature, we confirmed through thermal analyses that the chain conformation of macromolecules, adsorbed by one site on surface of CaCO_3 , changes from coil to linear, depending on the polymer surface density, as the study of PEO-SA adsorption

appears to demonstrate. On the other hand SEM analyses clearly evidence morphology modifications of CaCO_3 salt induced by PEO-SA. The results can be extended to carboxylate polymer plasticisers. TG/DTG analyses point out surface modifications too, being also able to select the changes of the surface amorphous to crystalline caused by different surface polymer concentrations.

From our point of view thermal analyses may contribute to understand the plasticiser–cement interaction, more specifically they can be useful to know the morphological modifications induced on ettringite that is the key intermediate in the cement hydration. We are now analysing the polymer–ettringite formation relation.

Acknowledgements

This work is supported by CTG S.p.A Centro tecnico di Gruppo-Italcementi.

References

- 1 A. M. Kjeldsen, R. J. Flatt and L. Bergström, *Cem. Concr. Res.*, 36 (2006) 1231.
- 2 R. J. Flatt, P. Bowen, A. Siebold and Y. F. Houst, *Proc. of 11th ICCI*, Durban, New Delhi, India 2003, pp. 676–685.
- 3 Y. F. Houst, P. Bowen and F. Perche, *12th ICCI*, Montreal, Quebec, Canada 2007, p. 12.
- 4 A. Pierre, J. M. Lamarche, R. Mercier and A. Foissy, *Cem. Concr. Res.*, 19 (1989) 692.
- 5 C. Comparet, A. Nonat, S. Pourchet, M. Mosquet and P. Maitresse, *Proc. of 7th CANMET/ACI*, V. M. Malhotra, Ed., Berlin, Germany 2003, pp. 195–210.
- 6 N. Mikanovic, K. Khayat, M. Pagé and C. Jolicoeur, *Colloid Surf. A: Physicochem. Eng. Aspects*, 291 (2006) 202.
- 7 M. Mosquet, Y. Chevalier, S. Brunel, J. P. Guicquero and P. L. Percec, *J. Appl. Polym. Sci.*, 65 (1997) 2545.
- 8 J. Fu, J. Fiegel and J. Hanes, *Macromolecules*, 37 (2004) 7174.
- 9 R. Atkin, V. S. J. Craig, E. J. Wanless and S. Biggs, *Adv. Coll. Interface Sci.*, 103 (2003) 219.
- 10 R. J. Hunter, *Foundation of Colloid Science*, 2nd Ed., Oxford University Press, Oxford, UK 2001.
- 11 I. C. McNeil and H. M. Musarrat, *Polym. Degrad. Stab.*, 49 (1995) 263.
- 12 J. P. Sanders and P. K. Gallagher, *Thermochim. Acta*, 388 (2002) 115.
- 13 N. B. Singh and N. P. Singh, *J. Therm. Anal. Cal.*, 89 (2007) 159.
- 14 N. Wada, U. Kanamura and T. Umegaki, *J. Colloid Interface Sci.*, 233 (2001) 65.

ICTAC 2008

DOI: 10.1007/s10973-008-9634-6