

Effect of waste polyethylene addition on the properties of white portland cement

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The effect of the addition of organic compounds (OC) an ordinary white Portland cement (WPC), on the properties such as compressive strength, fluidity, setting time, porosity and heat of hydration has been studied by adding 0.10-0.80 weight % of OC into the cement. The mixture of organic compounds obtained from a thermo-depolymerization of waste polyethylene (WP) and hydroxylation was composed by alcohols, alkenes and alkanes. The compressive strength was significantly dependent on the amount of OC. The highest value (45.3 MPa) was found by adding 0.35 wt.% of the OC. The porosity of the modified WPC did not change in the range 0-0.4 wt.% OC, however from 0.5-0.8 wt.% OC caused a linear increase of the porosity.

Key words: white portland cement, waste polyethylene, mechanical/thermal properties.

Introduction

There is a growing need for the recycling and reprocessing of plastic materials in order to reduce their environmental impact and optimize their commercial potential [1]. For instance, waste plastics can be converted into petrochemical feedstock with applications as recycled polymers, refined chemicals or fuels [2]. Current technologies for plastic reprocessing include thermal cracking and catalytic conversion [2-4]. The products of thermal cracking are gaseous and liquid hydrocarbons as well as solid residues. When the thermal cracking is carried out at low temperature (400-500 °C), the liquid fraction mainly consists of linear olefins and paraffins with C₁₁-C₁₄ carbon atoms and traces of aromatic compounds [5]. Due to the lack of a significant amount of aromatics, thermal cracking of waste plastics is not economically attractive and a catalytic conversion process is preferred [6]. Therefore, many attempts have been made in order to use waste polymers or organic compounds as admixtures in cement [7-17].

The beneficial effect of organic admixtures on the physical and mechanical properties of cement is well known and has been subject of extensive research [18, 19]. For instance, stabilization/solidification technology (SS) employs a large amount of waste (usually highly contaminated) to be entrapped in cement-based materials. By contrast, in the building industry a small amount of organic admixtures (0-5%) are used to improve the properties of the final products [20].

For instance, the incorporation of 0.20% of residues

of the sugar cane industry in cement results in delaying the hydration rate and a reduced amount of water in the process [7]. Furthermore, the workability is enhanced and the water absorption is decreased. Latex paint waste is another example of successful application in cement, due to a higher workability, higher flexural strength and a lower penetration of chlorine ions [8]. Therefore, the addition of a polymer can accelerate or delay the hydration reaction reducing the amount of water and then a modification in the mechanical properties is clearly detected. As reported by Singh and Singh [16], the improved properties of mortars and concretes in the presence of polymers are due to the interaction between the polymer and the cement, although, the nature of the interaction has not been clarified. Therefore, in this paper we studied the effect of organic compounds (OC) obtained from thermal cracking of waste polyethylene on the properties of white Portland cement during hydration reactions. The properties studied include the compressive strength, fluidity, setting time, heat of hydration and porosity using different amounts of OC and varying the hydration time.

Experimental

Materials

A commercial Type 1 WPC was used as a raw material for all tests. The chemical composition of the cement is given in Table 1. The main compounds were CaO, SiO₂ and Al₂O₃, SO₃ indicates the amount of calcium sulfate

Table 1. Chemical composition of the commercial WPC

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	Na ₂ O	K ₂ O	LOI*
%w	21.40	4.22	0.25	64.95	3.55	0.01	0.14	4.86

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added during the manufacture of the final product. As can be seen in Table 1, only impurities of Fe_2O_3 , K_2O and traces of Na_2O were found. The loss on ignition (LOI) (indicator of carbon content) was 4.86% and the insoluble residues only 0.22%. The particle size distribution of the WPC was obtained by using an analyzer of particle size (CILAs 1064 liquid) showing an average diameter of 10.73 μm . The mineralogical composition was determined by XRD (Siemens D5000 using $\text{K}\alpha_{\text{Cu}}$) and C_3S was the main compound with a triclinic structure (JCPDS 31-301 card), followed by C_2S (JCPDS 31-302 card) with a monoclinic structure and finally a small amount of C_3A (JCPDS 38-1429 card) with a cubic structure.

The organic compounds (OC) from waste polyethylene (WP) consisted of a mixture of alkanes, alkenes and alcohols (47.9, 37.4 and 14.7 wt.%, respectively) obtained by a two step synthesis; firstly, a pyrolysis reaction of WP forming alkanes and alkenes and secondly, a hydroxylation reaction using potassium permanganate forming a complex mixture of alcohols and residual alkanes and alkenes. The composition of the mixture was determined by GC/MS (PE, autosystem/turbomass) using a silica (0.25 μm , 30 m) capillary column. Fig. 1 shows the chemical structure of the main components of the mixture. The graded sand used was standard ASTM-C778.

Methods

In the case of fluidity, compressive strength and porosity tests, the samples of (WPC + OC) were prepared using 0, 0.10, 0.25, 0.35, 0.50, 0.60, 0.70 and 0.80 wt.% of OC and the amount of water was maintained constant at 11.5 wt.%, as well as the sand/WPC weight ratio which was 2.7. The OC was added to distilled water and it was mixed with a mechanical mixer before the hydration reaction. The fluidity test was carried out putting a conical

mold on the fluidity table (Humboldt, model MFG), then it was compacted and the mold was withdrawn to make the measurements. A caliper (Humboldt, model MFG) was used to determine the expansion, i.e., the sum of the four diameters spaced 45° from each other.

The compressive strength test was carried out using the standard analysis ASTM-C109/C109M, using cubic molds ($2 \times 2 \times 2 \text{ cm}^3$) where the paste was deposited and then kept them in a room with controlled temperature and humidity (Testo, model 171-2) for 24 h, then, the samples were withdrawn from the molds and placed in water. The measurements were performed at 1, 3, 7 or 28 days in a universal press (Ele international, model CT-7510) at a charge rate of 150 kg s^{-1} , reaching the maximum of charge in 20 to 80 s.

The porosity was determined by the Andrade method (ASTM C 642-06). This method consists in determining the oven-dry mass (A), then the saturated mass after immersion (B), then the saturated mass after boiling (C) and the immersed apparent mass (D). Then, make the following calculation: the volume of permeable pore space (voids), % = $(C - A)/(C - D) \times 100$

The setting time was determined according to the standard test ASTM-C 191-04b, using a Vicat apparatus (Humboldt, model MFG). In particular, the amounts of OC (wt.%) were similar to those mentioned above but the amount of water was 19.74 wt.% without sand addition and the mixture was prepared according to the mechanical mixing procedure of pastes (ASTM-C-305). The normal consistency test was carried out according to ASTM-C-187, all samples were also placed in a humid room and after 30 minutes a needle (1 mm diameter) was used to penetrate to 25 mm (initial setting time). The final setting time was fixed until no needle penetration was reached.

Measurements of the heat of hydration were carried out in an isothermal conduction- thermoelectric calorimeter (Seebeck Envelope Calorimeter) from the beginning of the reaction until 16 minutes of the hydration reaction time. The released heat curves were obtained according to the procedure of Adams [21].

Results and Discussion

Fluidity and compressive strength

The effect of OC addition on the fluidity of the WPC is shown in Table 2. In general, OC addition improves the fluidity of cement. The highest values of fluidity, 123% and 117.5% were found with 0.80 and 0.35 wt.% of OC added, respectively. This last value of fluidity also corresponds to the highest value of the compressive strength at 28 days, see Fig. 2. However, amounts of 0.50 wt.% of OC up to 0.80% caused a decrease in the compression strength. A significant increase of the compression strength, up to 47 MPa, is observed with 0.3 wt.% of OC added, at higher amounts of OC the compressive strength tends to decrease. For instance, if the wt.% of OC is 0.80, the compressive strength is 40 MPa but the

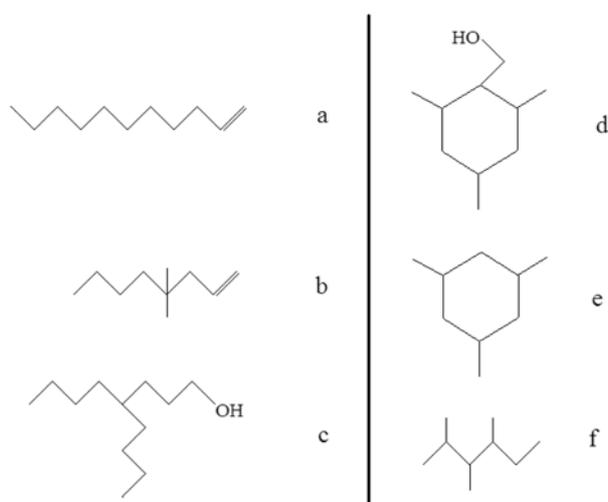
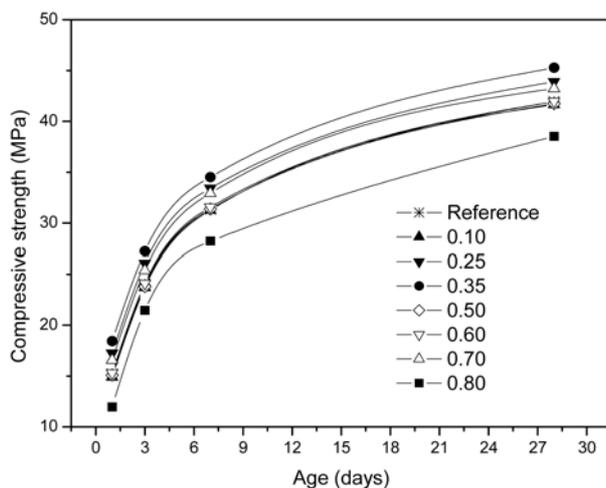


Fig. 1. Chemical structure of the main components of the organic compound (OC), obtained by GC/MS: (a). 1-docosene, (b). 4-dimethyl 1-heptene, (c). 2-butyl 1-octanol, (d). 2, 4, 6 trimethyl cyclohexyl methanol, (e). 1, 3, 5 trimethyl cyclohexane, (f). 2, 3, 4-trimethyl hexane.

Table 2. Effect of the OC added on the fluidity of the WPC

OC (%w)	Fluidity (%)
0	105.0
0.10	109.5
0.25	113.0
0.35	117.5
0.50	108.5
0.60	108.0
0.70	116.5
0.80	123.0

**Fig. 2.** Compressive strength results as a function of hydration time at different wt.% of OC.

fluidity is increased to 123%. If we compare these results with those of a reference (sample without addition of OC), a compressive strength of 42 MPa and fluidity of 105% are observed, it is clear that the organic addition has a beneficial effect on both, the compressive strength and fluidity.

Setting time

The setting time of cement and mixtures with the organic additive are given in Table 3. The values of the initial setting time and final setting time of cement were found to be 75 and 140 minutes, respectively. As is clearly seen in Table 3, the addition of the OC changes the setting time and acts as a retarder increasing the initial setting time from 84 to 235 minutes, in the range of 0.10-0.80 wt.% of OC added. The final setting time was also extended from 152 to 348 minutes for similar wt.% of OC added. As has been reported in other studies [7, 8, 22-24] the mechanism of set retardation is due to the chemisorption of the organic compound onto $\text{Ca}(\text{OH})_2$ nuclei and then retarding the hydration of C_3S . However, it may be also a chemical interaction between hydrated cement phases (C_3S , C_2S and C_3A) with the polar functional groups of the organic mixture that contributes to the whole retardation process [22-24]. Although, in this preliminary study we have no evidence about the formation of hybrid compounds

Table 3. Setting time of cement in the presence of organic compounds

OC (wt.%)	Setting time (min)	
	Initial	Final
0	75	140
0.10	84	152
0.25	140	239
0.35	170	245
0.50	177	270
0.60	183	283
0.70	229	301
0.80	235	348

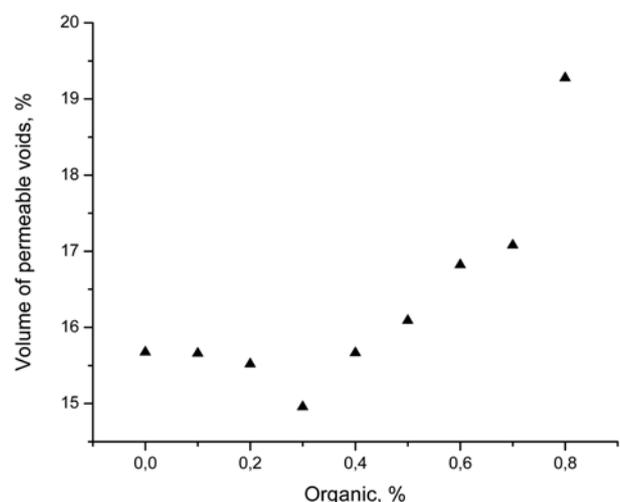
between organic compounds and the inorganic compounds of cement (from X-ray diffraction and FTIR, not shown here) the presence of the complex organic mixture coming from waste polyethylene is altering the progress of the hydration process [8].

Porosity

Fig. 3 shows that the addition of OC in the range 0-0.4 wt.% OC did not change the original porosity, however from 0.5-0.8 wt.% OC caused a linear increase of the porosity. Usually, the porosity of modified mortars decreases with the addition of polymer because the pores in the composite are filled up with the polymer [26]. However, it is believed that a significant portion of large pores found in concrete are formed according to a specific hydration mechanism [27].

Heat of hydration

As it is well known, when cement reacts with water, the process is connected by the evolution of heat, which leads to a decrease in the energy of the system [21]. A measurement of the heat evolved during hydration can be useful in order to understand the hydration process

**Fig. 3.** Porosity as a function of different wt.% of OC.

of cement because it is closely connected with the nature and reactivity of phases (C_3A , C_3S , C_2S), the rate of their interaction with water, the rate of formation of new phases and of course of their hardening structures.

The profiles of the heat of hydration at different reaction times and as a function of the amount of OC are shown in Figs. 4 and 5. In Fig. 4, the profiles show two peaks, associated with cement hydration. The initial peak appears after mixing the water with the cement, which is attributed to the dissolution and initial formation of ettringite. The second peak appears several minutes later (~300 minutes) and it corresponds to the hydration of C_3S which forms C-S-H and $Ca(OH)_2$. The highest second peak corresponds to the sample without OC and it is noted that the greater the amount of the OC added, the earlier this second peaks appears and then the amount of OC added seems to influence the rate at which hydration continues. Fig. 5 shows the initial peak of samples of cement with different wt.% of OC added, in all cases, the profiles followed the same behavior, at short reaction times, ca. 1 minute a clear

increase of the heat of hydration is observed. This part of the curves can be interpreted as unhydrated cementitious phases reaching a stabilization time. Note that the reference sample (without OC) showed the highest value of the heat of hydration at 1 minute. By increasing the amount of OC a lower values of the heat of hydration were clearly seen. During the heat releasing, between 1-14 minutes, the highest relative heat of hydration (measured from the maximum of the curve to the steady state at 14 minutes) was shown by the reference sample. By increasing the amount of OC added, the heat of hydration was diminished. This behavior could confirm the retarding effect of the OC on the hydration reaction. It seems that the tendency of cement to react with a small amount of OC is stronger at early hydration times (~2 minutes).

Water reduction

Table 4 shows the effect of OC addition on water reduction during hydration and on compressive strength after 1 day, maintaining a fluidity value of 110 ± 5 according to the standard ASTM C109/C109M-05. A slight decrease in the amount of water used is observed at 0.5 and 0.95 wt.% of OC. Note that only a 0.5 wt.% of water reduction was observed with respect to the reference sample (without OC). This small water reduction could be explained in terms of the presence of alcohols in the OC mixture. For instance, a commercial water reduction, such as lignosulfonates, causes a reduction in water consumption of around 5 to 10%. This has been explained in terms of the presence of lignosulfonates polar groups in their structure [26]. These polar groups are on the surface of the cement and sand and then, when they are in contact with water acquire a residual charge (i.e. positive for cement and negative for sand) avoiding cement particle agglomeration and stabilizing the air bubbles inside the mixture. It is known that to prevent cement particle agglomeration, during the formation of the suspension, a small amount of water must be used to obtain a good consistency [26]. This effect is caused by the adsorption of high molecular weight molecules with the hydrophilic groups (surfactants) on the surface of the cement, allowing repulsion between individual particles and consequently a reduction in friction. In summary, a water retard compound enhances the compressive strength without changing the workability of the cement.

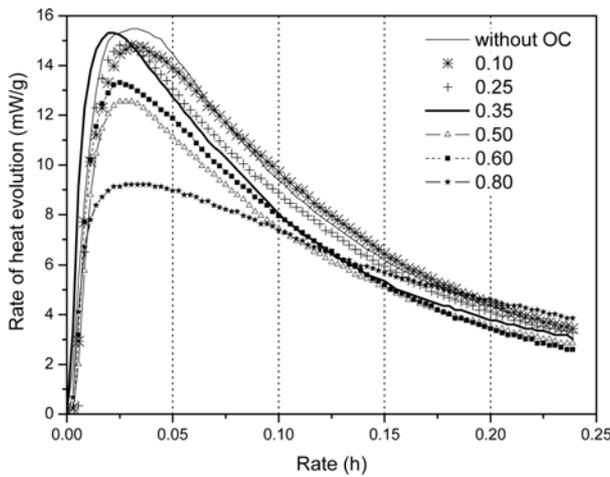


Fig. 4. Heat of reaction at early hydration times of WPC with different wt.% of OC.

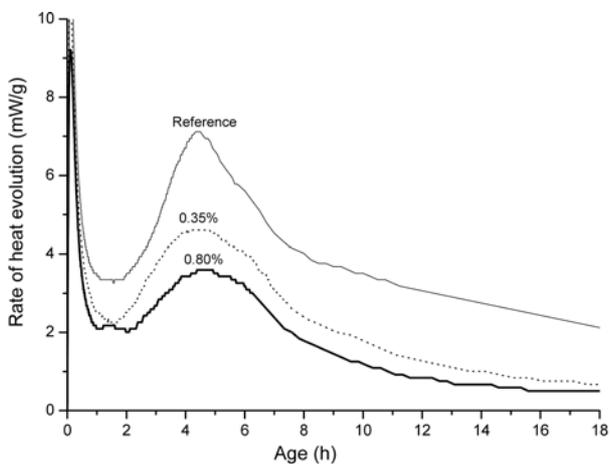


Fig. 5. Heat of hydration reaction during the hydration time of WPC at different wt. % of OC.

Table 4. Effect of the ratio OC/WPC on the water/WPC ratio And the compressive strength alter 1 day

OC/WPC (w/w)	Fluidity (%)	water/WPC (w/w)	Compressive strength (MPa)
0	109.0	0.496	15.0
0	105.0	0.492	15.5
0.02	108.5	0.492	15.4
0.02	111.0	0.480	15.3
0.04	107.0	0.472	14.5

Conclusions

The addition of organic compounds obtained by the depolymerization of waste polyethylene modifies the physical properties of the cement such as setting time, heat of hydration, water absorption, porosity and compressive strength of white Portland cement. The highest compressive strength and fluidity values were found at 28 days using a weight ratio of OC/WPC = 0.15 compared with the reference sample (without and organic addition). It may be concluded that a complex reaction mechanism between the organic compounds and water is carried out on the surface of the cement and sand allowing a significant enhancement in some properties of the WPC, however, more work is needed in order to explain in detail each effect.

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