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MDF CEMENTS
Synergy of the humidity and temperature effects

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Abstract

The applicability of MDF synthesis procedure, the coincidence of the interfacial cross-linking and the moisture resistance of MDF-related mixes based on two industrial Portland cements (CEM I, CEM II) and poly-P are reported. The knowledge of the moisture resistance of synthesized material is of paramount importance; two independent experimental methods confirmed that the moisture resistance of MDF cements based on CEM I (or CEM II) with 5% of poly-P achieves sufficient levels at 50% RH and at ambient values of RH. The results of thermal analysis are directly related to the former knowledge on the appearance and role of cross-links in the interfacial zone of MDF cements.

Keywords: cross-linked interface, MDF cements, moisture resistance, thermal analysis (TG/DTG)

Introduction

Cement chemistry notation: a short-hand notation based on 'constituent oxides', with abbreviations, is commonly used in cement chemistry in discussing the composition of clinkers and hydrated phases. Thus, in this paper $A=Al_2O_3$, $C=CaO$, $F=Fe_2O_3$, $H=H_2O$, $S=SiO_2$, $\bar{S}=SO_3$, $c=CO_2$, $AFm=C_4(A,F)\,\bar{S}H_{12}$.

MDF cement is a polymer-cement composite at the micrometer and nanometer levels, where the formation of atomic level cross-links is crucial for the technologically relevant properties. Crucial cross-linking section represents the interface, where oxygen-shared co-ordination of P, C, Al and Fe atoms secures the bonding of polymer to the AFm skeleton. The cross-links chemistry affects the porosity, microstructure and moisture resistance, the later being generally the key drawback of MDF cements.

MDF materials were first reported [1, 2] by the research group of Birchall at Imperial Chemical Industries (ICI, United Kingdom), the polymer being considered entirely as a rheological aid. Kendall *et al.* [1] attributed the high strength of these materials to the elimination of large critical flaws which reduce the strength of usual cast hydraulic cement pastes. It has been shown by Rodger *et al.* [3] and Popoola *et al.* [4] that the polymer phase preferably cross-links with Al in calcium aluminate–polymer composites. Thus, the polymer is likely a continuous phase and contributes itself to the

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strengthening process. Examples of the unique materials characteristics and potentialities span from reinforcement for ordinary cement pastes or mortars through thermal and sound insulators, formed body shells and armours, and to a cement-based shell for a solar powered car. Young [5] and Odler [6] have reviewed the knowledge on the chemical and mechano-chemical aspects of MDF materials, where the formation of atomic/ionic level cross-links is crucial for the technologically relevant properties. Our findings [7–12] have highlighted the future potential of blends of sulfo-aluminate-ferrite belitic clinker (SAFB), Portland cement (PC), hydroxy-propylmethyl cellulose (HPMC), or poly-phosphate glass (poly-P), key results being cited by Odler [6]. The level of moisture resistance of the compacted MDF tablets is determined by the atomic structure of the cross-links. The direct experimental evidence of the atomic structure of the cross-links is based on the results of MAS NMR spectroscopy, Mössbauer spectroscopy and thermal analysis also [7–9]. Cross-linked interfaces (formed through grafting of polymer chains to the grain surfaces) shield and partially prevent the unreacted clinker grains from secondary interactions [7, 8, 12, 13] in pressed tablets of MDF cements.

The paper tackles an applicability of MDF synthesis procedure, coincidence of the interfacial cross-linking and moisture resistance of MDF-related mixes based on two industrial Portland cements (CEM I, CEM II) and poly-P. The effects of varying levels of RH (50, 60, 70, 100%, ambient) of the environment upon the mass increase and phase changes of probes within studied system are evaluated of the gravimetric measurements and of the methods of thermal analysis.

Experimental

The raw materials for the MDF process and subsequent moisture treatment were: Portland cement (CEM I 42.5, CEM II/B-S 32.5R), poly-P of formula $(NaPO_3)_n$ and $Na_5P_3O_{10}$. The MDF processing sequence was as follows:

a) initial dry premixing of the cement followed by either

b) addition of poly-P powder (5% of total mass) and water to give water/solidus ratio *w/s*=0.2; or

c) addition of an aqueous solution of poly-P to incorporate 5% (by mass) of poly-P and to give *w/s*=0.2;

d) twin-rolling until the mixture reach the consistency of a dense dough (up to 5 min),

e) application of a static 5 MPa pressure in a pellet die of 10 mm for 30 min to 5 h, and

f) freezing of chemical reactions kinetically by air drying.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were conducted from 20 to 1000°C using a T.A.I. SDT 2960 instrument (powdered sample, mass 10–20 mg, heating rate 10°C min^{-1}, in flowing air). Thermal analysis of poly-P used and also of the cementitious samples free of inorganic polymer additive was reported and compared with the data in literature formerly [9, 14].

Moisture resistance was tested on cylindrical tablets kept in chambers with controlled relative humidity (RH) values of 50, 60, 70 and 100%, and subsequently, at ambient laboratory conditions. Mass changes are inversely proportional to the moisture resistance; mass changes were recorded by periodic weighing until constant mass defined equilibrium at the given RH. Equilibrium cumulative mass changes during the moisture uptake are compared with the mass of respective virgin sample, see in Table 1. TG/DTA measurements were conducted after the completion of the sequence of moisture exposures at 50 and 100% RH and after the laboratory atmosphere equilibration. TG/DTA measurements, when compared with data for fresh MDF probes, highlight phase changes and reactions on exposure to moist atmospheres. Further methodological details are given elsewhere [8, 11, 12].

Results and discussion

Our former studies indicated the advantage and prospectus of the mixes involving Portland cements and poly-P for the MDF cement properties, polymer and cement interact to create a unique atomic- and micro- structures with distinct characteristics. Present results display that the method of MDF synthesis is successfully applicable on mixes of CEM I/CEM II as with the powder so with the solution of poly-P. The knowledge of the moisture resistance of synthesized material is of paramount importance and will be discussed next.

Table 1 Equilibrium cumulative mass changes during the moisture uptake, as compared to the mass of respective virgin sample (100%)

MDF sample (synthesis conditions)	Mass increase (%) in the environment of				
	50% RH	60% RH	70% RH	100% RH	ambient
CEM I+5%poly-P, 0.5 h	*1.0*	*6.5*	*6.5*	*11.5*	*3.4*
CEM I+5%poly-P, 3.0 h	*0.8*	*7.0*	*8.0*	*14.2*	*3.8*
CEM I+1%poly-P, 0.5 h	0.5	6.5	9.0	12.5	8.7
CEM II+5%poly-P, 0.5 h	*1.7*	*7.5*	*8.5*	*11.0*	*2.0*
CEM II+5%poly-P, 3.0 h	*1.4*	*6.5*	*6.5*	*9.5*	*2.8*
CEM II+1%poly-P, 0.5 h	0.8	6.0	7.0	8.0	4.9

The results summarized in Table 1 show *i*) samples are sufficiently resistant in the environment of 50% RH; *ii*) the environments of 60–100% RH exert step-wise negative effect, mass changes increase, however, are partly reversible as shown of *iii*) mass change – moisture uptake in the ambient RH decreases; *iv*) the reductions of mass change – moisture uptake in the ambient RH, due to interfacial cross-linking and impregnation of the virgin MDF cement [6, 11, 13], achieve appropriate levels only in samples containing 5% of poly-P (shown in Table 1 in italics).

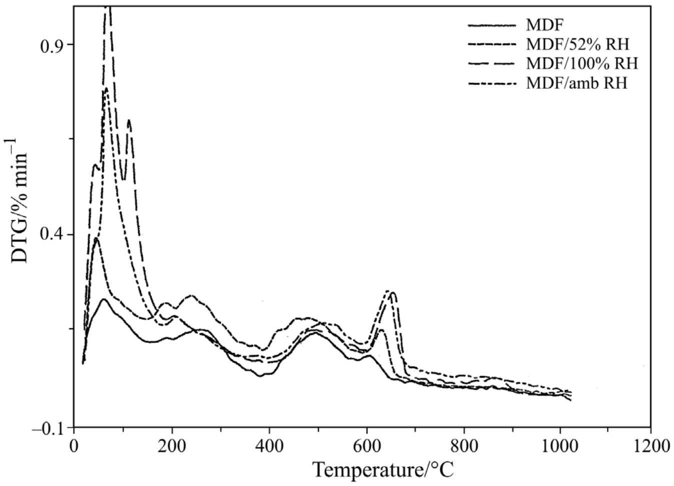

Fig. 1 DTG curves indicating the temperature intervals of four decomposition steps with distinguishable mass losses; topical MDF composition is based on the mix CEM II+5% poly-P, state of the probe before decomposition (virgin *vs*. moisture treated) see in the line's legend inside the figure

The cumulative mass changes represent the sums of a series of mass and phase changes, as shown earlier [9, 11, 14] and also here by thermal analysis. Indicative mass and phase changes have been attributed based on four decomposition steps evident in DTG curves of virgin and also moisture attacked MDF probes (Fig. 1), and are as follows:

a) 20–220°C, an interval of cementitious hydrates decomposition [9, 15],
b) 220–350°C, an interval of the cross-links decomposition [9, 11, 14],
c) 400–550°C, an interval of the decomposition of portlandite [9, 15] and
d) 550–800°C, an interval of the decomposition of calcite [9, 11, 15, 16].

The quantification of the contents of hydrated and cross-linked phases in virgin and also moisture attacked MDF probes was deducted of TG curves (Table 2). Moisture uptake is accompanied by the increase of the content of cementitious hydrates and calcite (cf. steps a, d of the decompositions, Fig. 1 and Table 2). The contents of cross-linked phase (step b) and portlandite (step c), in contrast, are kept nearly constant. The values for step b in samples with 1% of poly-P confirm an insufficient level of cross-linking and surface impregnation of MDF probes with low content of poly-P. The aspects of possible fragmentation/depolymerization of the $(NaPO_3)_n$ chains due to the grafting have been discussed elsewhere [6, 8, 9] and are included in the atomic level model of the formation and role of cross-linked interfaces in the system. The presented thermoanalytical knowledge on phase changes confirm the vital role of cross-links in MDF cements [5–7, 12, 13] and support the indication (above in this paper) that interfacial cross-linking and impregnation of the virgin MDF cement achieve appropriate levels in samples containing CEM I or CEM II with 5% of poly-P only.

Table 2 Decomposition steps and relative mass changes, as determined by TG

MDF sample (synthesis condition)	Step of decomposition	Relative mass decrease (%) of			
		MDF virgin	MDF attacked by the environment of		
			50% RH	100% RH	ambient
	a				
CEM I+5% poly-P, 3 h		4.05	n/a	n/a	8.0
CEM II+5% poly-P, 3 h		3.0	4.3	9.3	8.8
CEM II+1% poly-P, 0.5h		4.65	4.1	5.75	7.6
	b				
CEM I+5% poly-P, 3 h		1.95	n/a	n/a	1.9
CEM II+5% poly-P, 3 h		1.8	2.8	1.5	1.4
CEM II+1% poly-P, 0.5 h		1.2	2.45	1.15	1.35
	c				
CEM I+5% poly-P, 3 h		2.4	n/a	n/a	2.4
CEM II+5% poly-P, 3 h		1.7	2.8	2.2	2.5
CEM II+1% poly-P, 0.5 h		2.7	1.2	1.0	2.5
	d				
CEM I+5% poly-P, 3 h		2.5	n/a	n/a	3.05
CEM II+5% poly-P, 3 h		0.7	1.0	1.7	2.1
CEM II+1% poly-P, 0.5 h		1.5	0.9	1.9	4.0

Conclusions

- The method of MDF synthesis has been successfully applied on mixes of CEM I/CEM II as with the powder so with the solution of poly-P.
- Two independent experimental methods confirmed the resistance of MDF cements in the environment of 50% RH. The moisture resistance of MDF cements based on CEM I (or CEM II) with 5% of poly-P achieves sufficient level also at ambient values of RH.
- Relative changes of the contents of hydrates and cross-links after the interactions of studied materials with the moisture have been estimated from results of thermal analysis. The results directly relate to the knowledge on the appearance and role of cross-links in the interfacial zone of MDF cements.

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