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Optimization of material characteristics of macro-defect free cement

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ABSTRACT

Macro-defect free (MDF) cement is a high-strength cement–polymer composite produced by mixing cement (commonly calcium aluminate cement) with small amounts of polymer (commonly polyvinyl alcohol acetate) and water, applying high shear, and finally applying relatively low pressure (about 5 MPa) and modest temperature (about 80–100 °C). However, MDF cements lose considerable strength when exposed to water. The objective of this study was to explore the effects of cement and polymer compositions on flexural strength and water sensitivity. Calcium aluminate cements were used with Al_2O_3 contents between 42% and 79%. Production of MDF cement was successful with all cements, but the highest strength (268 MPa) was obtained with 70% Al_2O_3 cement. Secondly, PVAs were used that differed in their degree of hydrolysis between 73% and 99%. Of these, the one with a moderate degree of hydrolysis produced the highest strength (228 MPa). All mixtures had strength loss on exposure to water, but PVAs with moderate degrees of hydrolysis exhibited the lowest strength losses (50–60%).

1. Introduction

A new cement–polymer composite, named macro-defect free (MDF) cement, was developed and patented by Birchall et al. [1,2]. The composite has a very high strength, especially tensile strength, attributed to its low porosity, a result of the very low water/cement ratio, and crosslinking between polymer and cement, a result of the unique composition and production process. The composite is prepared from cement and small amounts of polymer and water. The mixture is processed using a method inspired from rubber production in which the elastic–plastic mixture is repeatedly passed between two roller mills. High shear forces during this process eliminate voids. The sheet is then pressed under modest pressure and temperature and finally cured at a modest temperature.

The most important property of the composite is its remarkably high flexural strength, 20 or 30 times higher than conventional (plain) cement pastes. Flexural strength values of 150–300 MPa are easily achieved, close to that of ordinary steel. Table 1 shows some mechanical properties of ordinary Portland cement (OPC) and MDF cement systems. The inventors of the composite attributed this high flexural strength to the elimination of macro voids during processing, as noted above, and for this reason named it macro defect free cement; they further claimed that the polymer is merely a rheological aid. However, later studies [3–6] showed that crosslinking reactions between polymer and cement play an important role in the achievement of high strengths. Furthermore, applying hot pressing accelerates crosslinking and also causes a dense compaction. Therefore, the material is also defined as organo–cement composite or polymer–cement composite.

The cement generally comprises more than 80% by weight of the composite. Calcium aluminate cement (CAC) is usually preferred over OPC because it provides higher flexural strength levels. Birchall et al. [2] proposed that water soluble or redispersible polymers are most suitable for use in MDF cement. Poly(vinyl alcohol-co-vinyl acetate) (PVA) copolymers [2,9], poly(acrylamide) [10,11] and cellulosic products [12–16] are usually preferred. However, others [17–20] succeeded in producing MDF cements with alcohol soluble polymers such as phenol resin precursors. In addition, glycols (especially glycerol) are often used as plasticizers. Of the various cements and polymers that have been studied, combinations of CAC and PVA copolymers provide the highest strength, and have therefore been studied the most. The main hypothesis of chemical interaction between the cement and polymer, shown in Fig. 1, is that the hydroxyl groups of PVA are crosslinked with the aluminate ions ($[Al(OH)_4]^-$) released during the hydration reaction of cement, similar to the PVA-borate ion ($[B(OH)_4]^-$) crosslinking reaction [3–6].

In spite of their remarkably high flexural strengths, MDF cements lose considerable strength on exposure to water, including vapor. This water sensitivity limits commercial usage of the composite. Physical deterioration of specimens stored in water starts in a few days and the composites sometimes lose more than half

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Table 1
Some typical values of mechanical properties for OPC and MDF cements.

Property	OPC	MDF[a]
Flexural strength, MPa	5–10	150–300
Compressive strength, MPa	40–60	380
Young's modulus, GPa	20–30	40–50

[a] CAC-PVA MDF cement [7].

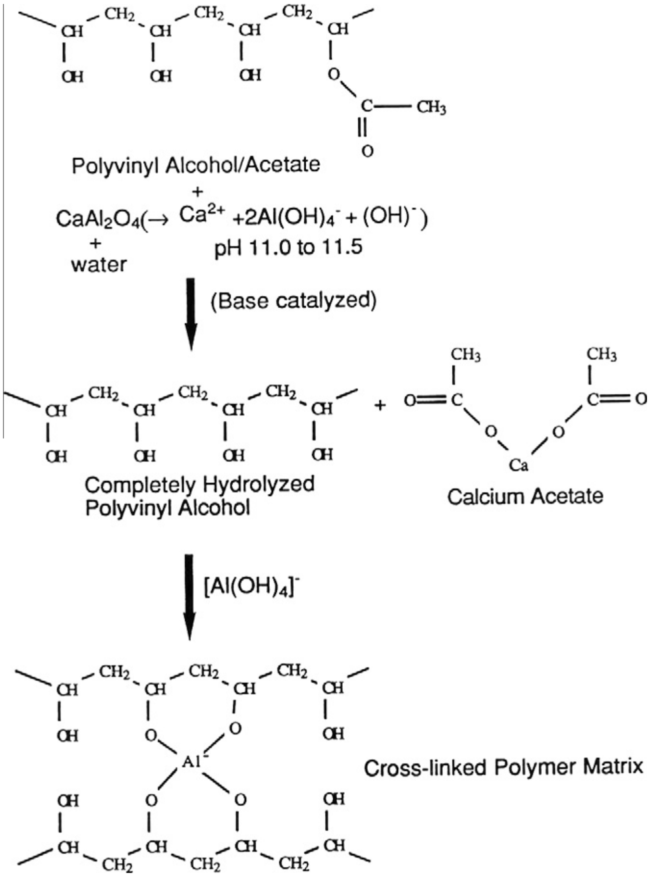

Fig. 1. Proposed chemical reactions in formation of MDF cement from CAC and PVA [8].

of their initial strength in only few weeks. Much research has focused on the water sensitivity. Some additives to reduce the water sensitivity have been studied, such as alkali metal silicates [21], alumina [22], cross linking chemicals [8,23,24], gypsum [25], $CaCl_2$ and $ZnCl_2$ [11], silica fume [9] and activated carbon [26,27]. Russell [7] increased polymer crystallinity and reduced the polymer content. Atkinson and Walsh [28] stored MDF cements in boric acid solution. Although none of these studies successfully eliminated the moisture sensitivity, they provided a better understanding of MDF cements.

In this study, the effects of cement and polymer composition on strength and water sensitivity of CAC-PVA MDF composites were investigated. Although cements with 70% Al_2O_3 are generally preferred for the production of MDF cement [2,5,7,8,29,30], not enough is known about the effects of cement Al_2O_3 content on strength and water sensitivity; therefore, CACs with Al_2O_3 contents ranging from 42% to 79% were used in these experiments. Regarding PVA, the general understanding is that the degree of hydrolysis (DH) and degree of polymerization (DP) are the most important characteristics, that moisture absorption is affected more by DH than by DP, that PVAs with a higher DH have less ability to absorb moisture, and that PVA solubility decreases with increasing DH [31]; for this reason, the PVAs with a DH ranging from 73% to 99% were tested. On the other hand, PVA solubility decreases with increasing DH, therefore, heating process was applied to increase the solubility of PVAs with high DH.

2. Experimental studies

2.1. Materials

The study utilized four CACs (supplied by Lafarge North America, Chesapeake, Virginia, USA) whose alumina contents ranged from 42% to 79%. Chemical compositions of the cements are given in Table 2.

The study also utilized nine PVA copolymers (supplied by Marubeni America Corporation, NY, USA and Nippon Gohsei Europe GMBH, Duesseldorf, Germany) whose degree of hydrolysis ranged from 73% to 99%. Properties are given in Table 3. One PVA (N 300) was fully hydrolyzed, and four (KP 08R, NK 05R, KH 17 and GH 20) were partially hydrolyzed. The others were modified with some functional group like carboxyl or acetoacetyl to make them more soluble.

2.2. MDF cement production

Production of MDF cements using two roller mills was first proposed by Birchall et al. [1,2] and later optimized by Russell [7], and the latter method, with some modifications, was used in this study. Cement, polymer and water were added separately into a planetary mixer and processed to form a damp, crumbly mixture. The mixture was then passed repeatedly between two roller mills (Fig. 2), folding and changing the direction each time, to eliminate the large voids. The gap, speed of rollers, and number of passes were set to provide maximum strength (details are provided in [32]). The processing disperses the cement grains in the polymer matrix and rapidly produces a rubbery, cohesive dough. The dough was subsequently calendered into a flexible sheet, also using two roller mill, and cured in a hot press at 80 °C and 5 MPa for 10 min followed by 24 h storage in oven at the same temperature.

The process was modified for PVAs with high DH. To increase solubility, they were first mixed with water and heated (to a temperature in the range 70–90 °C, depending on the DH of PVA) as suggested by Finch [31] and the catalog of Nippon [33]. However, this modification did not improve processability or strength.

After curing, ten circular specimens (approximately 32 mm diameter) were drilled from each sheet (approximately 1.7 mm thick) with a diamond hole saw. Half the specimens were stored in water and the other half were stored in a desiccator over silica gel until testing.

2.3. Proportions

In one experiment, MDF cements were produced using four different calcium aluminate cements (Table 2) and one partially hydrolyzed PVA copolymer, KH 17 (Table 3). Mix proportions of these MDF cements are given in Table 4. The polymer/cement ratio (p/c, by weight) was kept constant at 0.07 for all mixtures; however water/cement ratio (w/c, by weight) was changed between 0.09 and 0.19 in order to obtain a paste suitable for production. A total of 28 batches (7 batches with each cement) was prepared. The batches were coded with respect to w/c.

In another experiment, MDF cements were produced using nine different PVAs (Table 3) and one cement (Secar 71, Table 2). Compositions for $w/c = 0.11$ and $p/c = 0.07$ are given in Table 5. The w/c

Table 2
Compositions and properties of calcium aluminate cements[a] used in the production of MDF cement.

Cement	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	SiO_2 (%)	Surface area[b] (cm^2/g)	Density (g/cm^3)
Ciment Fondu	42.29	35.05	14.05	4.52	4033	3.13
Secar 41	48.86	34.89	7.16	5.56	4249	3.00
Secar 71	70.0	29.2	[c]	[c]	3986	2.93
Secar 80	78.95	19.57	[c]	[c]	>8000	3.07

[a] Provided by the manufacturer.
[b] Measured using Blaine method.
[c] Not provided.

Table 3
Properties of PVAs[a] used in the production of MDF cement.

Product name	Degree of hydrolysis (mole%)	Viscosity of 4% solution (MPa s)	pH	Feature
KP 08R	72.6	6.4	5.4	Partially hydrolyzed
NK 05R	73.2	4.8	5.4	Partially hydrolyzed
KH 17	79.6	36.2	5.5	Partially hydrolyzed
GH 20	87.1	46.5	5.5	Partially hydrolyzed
Z 320	92.7	22.3	4.7	Acetoacetylated
T 330	96.0	30.0	7.0	Carboxylated
Z 410	97.9	51.7	4.9	Acetoacetylated
N 300	98.4	27.8	5.9	Fullly hydrolyzed
Z 100	99.1	5.4	5.0	Acetoacetylated

[a] Provided by the manufacturer.

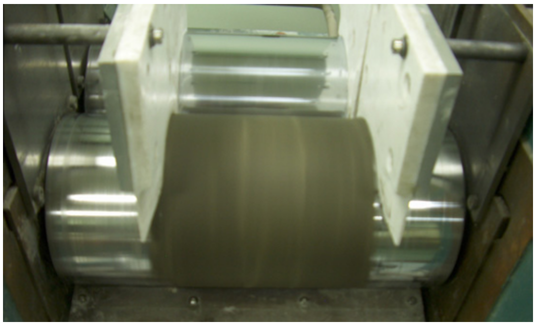

Fig. 2. MDF cement production with two roller mills.

Table 4
Mix proportions of MDF cements with different cements.

Material	Weight		Volume	
	(g)	(%)	(cm^3)	(%)
Cement	150	79–86	51.2	58–70
PVA	10.5	6	8.1	9–11
Glycerol	1.05	1	0.8	0.9–1.1
Water	13.5–28.5	8–15	13.5–19.5	18–32
Total	175–190	100	74–89	100

Table 5
Mix proportions of MDF cements with different PVAs.

Material	Weight		Volume	
	(g)	(%)	(cm^3)	(%)
Cement	120	84.2	40.96	67
PVA	8.4	5.9	6.46	10
Glycerol	0.84	0.6	0.67	1
Water	13.2	9.3	13.20	22
Total	142.4	100	61.3	100

ranged from 0.11 to 0.20 in order to obtain a paste suitable for production. The *p*/*c* was generally 0.07 but was decreased to 0.04 or 0.05 in some cases. A total of 51 mixtures was prepared. Mixtures were coded with respect to *w*/*c*, *p*/*c* and whether the polymer–water mixture was heated (for example, 11-7* is *w*/*c* 0.11 and *p*/*c* 0.07, and * means the PVA solution was heated). Mixtures with the same mixture code were repeated to assess reproducibility.

2.4. Testing procedures

Tests for biaxial flexural strength were carried out on specimens both dry and exposed to water at 7 and 28 days in accordance with ASTM F-394 [34]. An Instron universal testing machine equipped with a 1-kN load cell was used. The cross-head speed was 0.5 mm/min.

X-ray diffraction (XRD) analyses were conducted on powdered specimens using a Rigaku powder diffractometer. Patterns were analyzed qualitatively using computer software (Jade) and a standard data file (Powder Diffraction File). Simultaneous thermogravimetric analysis (TG) and differential thermal analysis (DTA) tests were conducted on powdered specimens using a Netzsch model STA 409. Fourier transform infrared (FTIR) spectra were obtained on pieces of MDF cements using a Perkin–Elmer spectrophotometer. Water absorption was measured on MDF cements produced using selected *w*/*c* levels, as explained in Section 3.6, for each PVA at 7 and 28 days.

3. Test results and discussion

3.1. MDF cement production

For *w*/*c* levels up to 0.13, four passes through the roller mill were enough to produce a uniform sheet. Mixtures with higher *w*/*c* levels became more rubbery and pliable but were difficult to remove from the roller mills, so they had to be passed through the mills several more times and production times were longer. It was impossible to prepare MDF cement sheets in 5 batches at low *w*/*c* (49-09, 79-09, 79-10, 79-11 and 79-13) due to lack of coherence. Some MDF cements are shown in Fig. 3. Lower Al_2O_3 cement produced darker MDF cements.

Fig. 3. MDF cements produced with different CACs.

Production was successful with 5 of the 9 PVAs listed in Table 3. Successful MDF cement specimens, such as the one prepared with a partially hydrolyzed PVA (KH 17) in Fig. 4a, were cohesive and smooth. Production was not successful with fully hydrolyzed PVA (N 300) or with carboxylated PVA (T 330), even when the PVA solution was heated, regardless of w/c or p/c. In addition, MDF cements could not be produced with low hydrolysis PVAs (KP 08R and NK 05R). It was very hard to pass these materials between the rollers and the mixture temperatures increased during rolling. Unsuccessful pastes had edges that were crumbly, cracked, and tore easily, and they often debonded from the faster roller and knitted poorly during calendering. One example of unsuccessful products is shown in Fig. 4b. It seems that it is not possible to produce MDF cements with PVAs at low hydrolysis degrees, such as 73.2% and lower. Similarly, Birchall et al. [2] tried PVAs with DH as low as 50% but were unsuccessful in producing MDF cement. At high hydrolysis degrees, it was reported that the production is possible for only low molecular weights [9]. In the present study, the fully hydrolyzed PVA (N 300) did not allow successful production of MDF, perhaps because it has comparatively high viscosity and presumably high molecular weight. However, the acetoacetylated PVAs at both low and high viscosities (Z100 and Z 410) allowed successful productions showing that the attachment of acetoacetyl groups is more important than molecular weight at high hydrolysis degrees.

On the other hand, specimens produced with heating the PVA to enhance dissolution had smoother surfaces than the specimens produced without heating.

Each PVA showed different characteristics that required changes in w/c. The w/c values were selected based on results and observations during production. Selected w/c values for each PVA are given in Table 6.

Table 6
Selected w/c values for MDF cements produced with different PVAs.

Polymer	KH 17	GH 20	Z 320	Z 410	Z 100
w/c	0.11	0.13	0.15	0.20	0.15

3.2. Biaxial flexural strength

3.2.1. Production of MDF cements with different CACs

Biaixal flexural strength test results are shown in Fig. 5 for 7 days and Fig. 6 for 28 days. The Al_2O_3 contents increase from left to right. Dry strength refers to specimens stored over silica gel and wet strength refers to specimens stored in water.

The highest dry strengths, about 250 MPa at 7 days and 270 MPa at 28 days, were obtained using the cement with 70% Al_2O_3. Nearly all batches prepared with this cement gave higher flexural strengths when compared with other cements at the same w/c ratio. Similar dry strengths were obtained using cements with 49% and 42% alumina. The lowest dry strengths, about 85 MPa at 7 days and 100 MPa at 28 days, were obtained with 79% Al_2O_3. It was difficult to process MDF cement with this cement even at high w/c, perhaps due to its high fineness (Table 2), which may require a higher water content to wet the cement particles (see Fig. 7).

Dry strengths were very similar at the two ages, 7 days and 28 days. Calcium aluminate cements are known to develop strength quickly, and it is obvious that the MDF cements have nearly reached their highest flexural strengths at 7 days. However, their wet strengths continued dropping up to 28 days and the strength loss at 28 days was almost double that at 7 days.

It seems that there is an optimum w/c around 0.10–0.11 with respect to dry strength results for cements with Al_2O_3 contents of 70% and lower. At higher w/c, strength is lower due to the higher pore volume, similar to the traditional concretes. However, at lower w/c, strength is also lower, probably due to the inadequate workability. On the other hand, for MDF cements prepared with 79% Al_2O_3, the production was more difficult, only possible for w/c 0.15 and higher, and the samples had poor strength due to the insufficient mixing and compaction as well as higher pore volume.

Reductions in strength were consistently observed during wet storage. At 7 days, the reduction in wet strength ranged from 15% to 50% for MDF cements with alumina content 70% and lower. Smaller reductions were generally obtained for w/c 0.11–0.15, and larger reductions at lower and higher w/c. The reduction in strength was much higher (48–83%) for MDF cement with 79% Al_2O_3 content than those with lower alumina content. At 28 days, the reduction in wet strength averaged about 60%, larger for the cement with 79% Al_2O_3. As shown in Fig. 8, strength reduction was

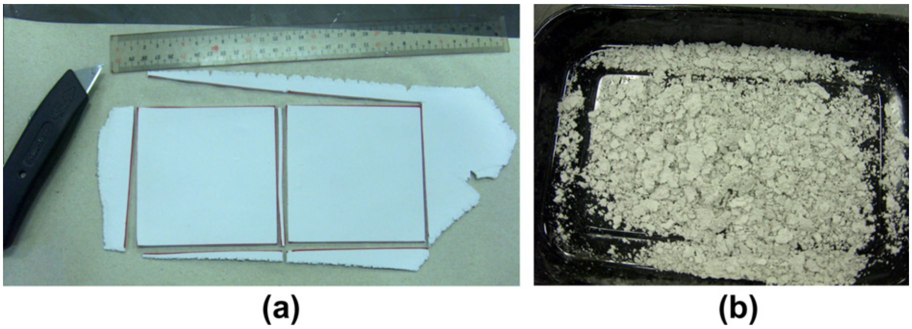
(a) (b)

Fig. 4. MDF cement production with (a) partially hydrolyzed PVA (KH 17), w/c 0.11, and p/c 0.07 and (b) fully hydrolyzed PVA (N 300), w/c 0.30, and p/c 0.05.

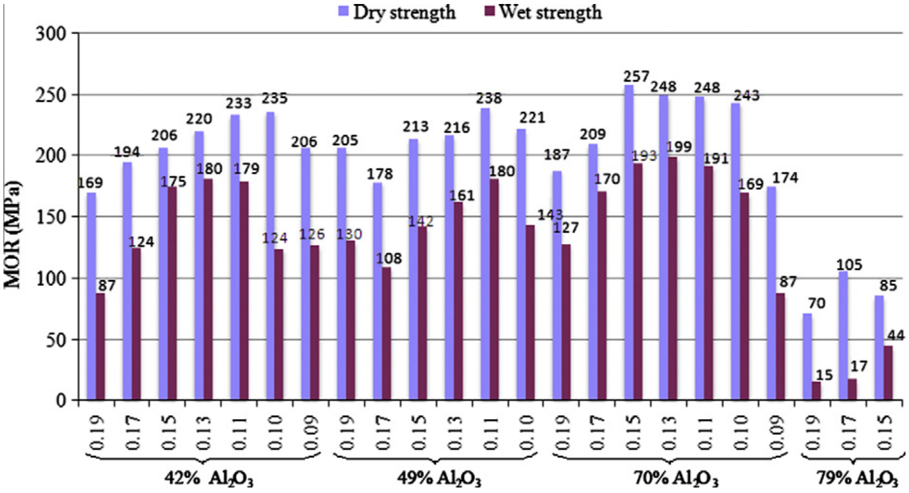

Fig. 5. Biaxial flexural strength values at 7 days (the numbers in the *x*-axis show *w*/*c*).

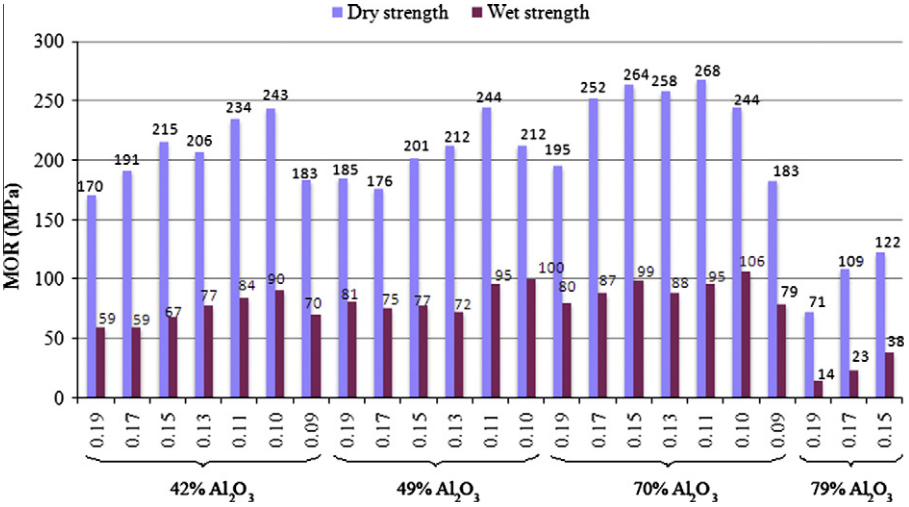

Fig. 6. Biaxial flexural strength values at 28 days (the numbers in the *x*-axis show *w*/*c*).

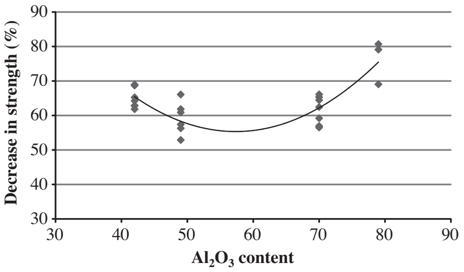

Fig. 7. Strength reduction at 28 days water storage versus Al_2O_3 content.

slightly smaller at intermediate Al_2O_3 contents. Delucchi and Cerisola [35] reported that the higher the alumina content the lower the porosity and the lower the swelling degree during immersion in water, however their highest alumina content was 70%.

3.2.2. Production of MDF cements with different PVAs

Biaxial flexural strength tests were conducted on the specimens at 7- and 28-day ages. Results at 7 days can be seen in Table 7. Wet and dry flexural strengths of specimens are shown at 7 days in Fig. 8 and at 28 days in Fig. 9. The PVA hydrolysis degree increases from left to right in these figures. Mixtures 11-7 for GH 20 and 17-5 for Z 410 were tested only at 7 days. The highest dry strengths, about 200 MPa at 7 days and 230 MPa at 28 days, were obtained using partially hydrolyzed PVAs (KH 17 and GH 20). The lowest dry strength at 7 days, 41 MPa, was also obtained using the partially hydrolyzed PVA GH 20, but at a lower *w*/*c*. The lowest dry strength at 28 days, 67 MPa, was obtained using the acetoacetylated PVA (Z 410).

As observed in the experiments using different cements, dry strengths were very similar at the two ages, 7 days and 28 days. Some mixtures were slightly higher at 28 days, but some were slightly lower. The mixtures using different cements showed a clear trend with *w*/*c*, but the mixtures with various PVAs covered a more narrow range in *w*/*c* so no trend could be discerned.

The reduction in strength on water storage at 7 days ranged from 9% (17-7 with Z 410) to 80% (15-7 with Z 100). The former result, obtained with acetoacetylated PVA, was very promising. However, the reduction was 60% at 28 days for this specimen. At 28 days, the reduction in strength ranged from 53% (13-5 with GH 20) to 82% (15-7 with Z 320). The strength reductions were greater (70% or more) for highly hydrolyzed PVAs (Z 320, Z 410 and Z 100) and lesser (about 50–55%) for partially hydrolyzed PVAs (KH 17 and GH 20). However, the MDF cement with highly hydrolyzed PVA had very

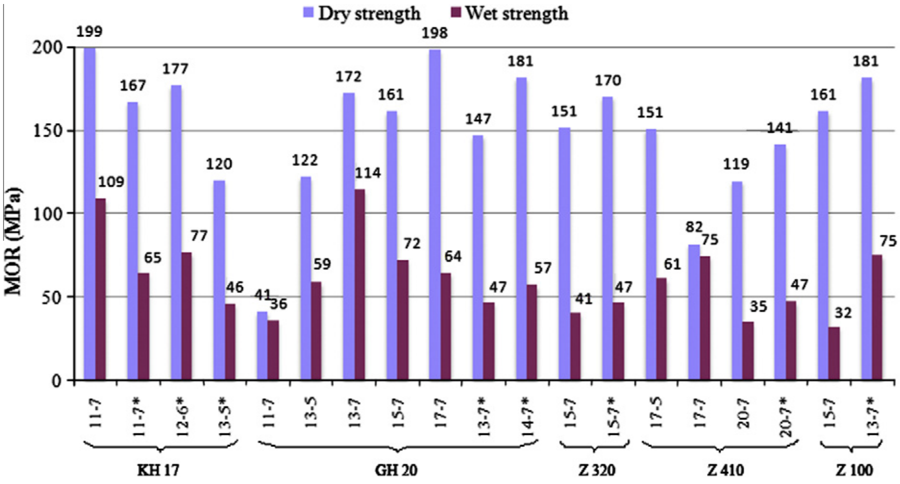

Fig. 8. Dry and wet strengths of MDF cements produced with different PVAs at 7 days (the numbers in x-axis show w/c and p/c, $*$ polymer was heated during mixing).

Table 7
Biaxial flexural strength values at 7 days for MDF cements prepared with different polymers.

Mixture no.	Polymer type	Mixture code	w/c	p/c	Dry strength			Wet strength		
					$\bar{S}$ (MPa)	σ (MPa)	V (%)	$\bar{S}$ (MPa)	σ (MPa)	V (%)
1	KH 17	11-7	0.11	0.07	199	31	16	109	47	43
2		11-7[a]	0.11	0.07	167	49	30	65	3	5
3		12-6[a]	0.12	0.06	177	12	7	77	41	53
4		12-4[a]	0.12	0.04	120	5	4	46	2	4
5	GH 20	11-7	0.11	0.07	41	6	15	36	5	13
6		13-5	0.13	0.05	122	37	31	59	1	2
7		13-7	0.13	0.07	172	35	21	114	16	14
8		15-7	0.15	0.07	161	28	18	72	15	21
9		17-7	0.17	0.07	198	26	13	64	18	27
10		13-7[a]	0.13	0.07	147	36	25	47	9	18
11		14-7*	0.14	0.07	181	10	6	57	1	2
12	Z 320	15-7	0.15	0.07	151	25	16	41	6	14
13		15-7[a]	0.15	0.07	170	10	6	47	59	126
14	Z 410	17-5	0.17	0.05	151	51	34	61	2	3
15		17-7	0.17	0.07	82	7	8	75	9	11
16		20-7	0.20	0.07	119	19	16	35	5	14
17		20-7[a]	0.20	0.07	141	23	16	47	4	8
18	Z 100	11-7	0.11	0.07	Impossible to obtain in sheet form					
19		15-7	0.15	0.07	161	18	11	32	5	15
20		13-7[a]	0.13	0.07	181	8	5	75	12	15
21		15-7[a]	0.15	0.07	Impossible to obtain in sheet form					
22–28	T 330	–	0.11–0.25	0.05–0.07	Impossible to obtain in sheet form					
29–35	N 300	–	0.15–0.30	0.05–0.07	Impossible to obtain in sheet form					
36–43	KP 08R	–	0.11–0.25	0.07	Impossible to obtain in sheet form					
44–51	NK 05R	–	0.11–0.25	0.07	Impossible to obtain in sheet form					

[a] Polymer was heated during mixing.

smooth surfaces with no visible degradation during water storage, contrary to the MDF cements with partially hydrolyzed PVAs.

On the other hand, although processing of PVA by heating resulted in smooth surface no significant difference in strength or water sensitivity was observed, as can be seen in Table 7.

3.3. XRD analyses

MDF cements produced with the four calcium aluminate cements (42-11, 49-11, 70-11 and 79-17) and the four unhydrated cements (Table 2) were analyzed using XRD. The pattern for 70-11 is shown in Fig. 10. The mixture contains only CA ($CaO{\cdot}Al_2O_3$) and CA_2 ($CaO{\cdot}2Al_2O_3$) phases, which were also seen in the unhydrated calcium aluminate cement. Neither sample showed a peak attributable to any hydration product. It appears that the PVA has prevented the formation of crystalline hydration products. The same observation was reported by previous researchers [5,9,12,36–38].

3.4. FTIR analyses

The FTIR analyses were conducted on 1-year-age MDF cements (70-11 and 79-17) mading using two cements (70% and 79% Al_2O_3) and one PVA (KH 17). The PVA (in powder form) was also analyzed. The FTIR spectra were normalized and major vibration bands were assigned to chemical groups. The purpose of these tests was to seek evidence of polymer crosslinking in MDF cement. Spectra with peak assignments are shown in Fig. 11.

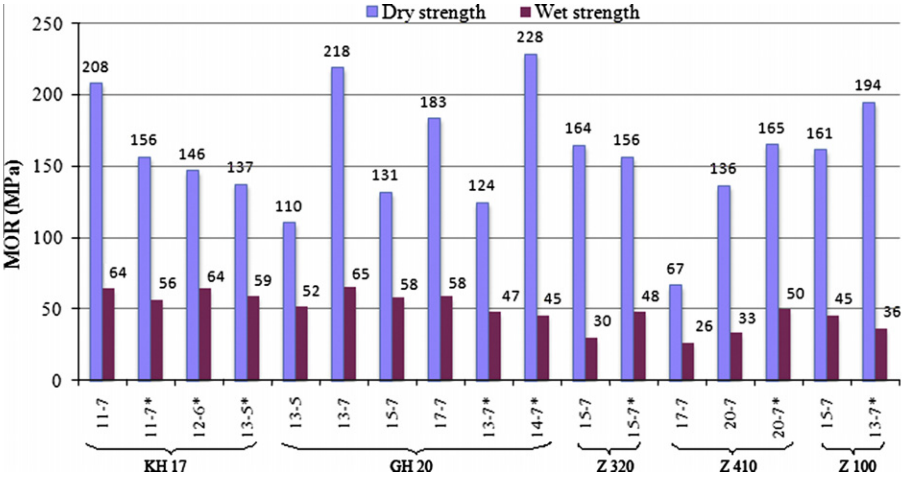

Fig. 9. Dry and wet strengths of MDF cements produced with different PVAs at 28 days (the numbers in *x*-axis show *w*/*c* and *p*/*c*, ∗ polymer was heated during mixing).

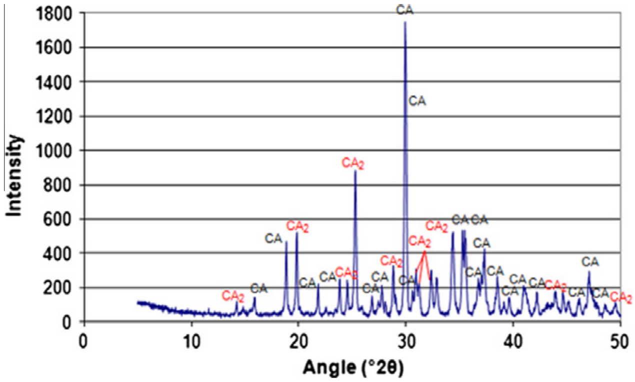

Fig. 10. X-ray diffraction spectrum of MDF cement with 70% Al_2O_3 cement.

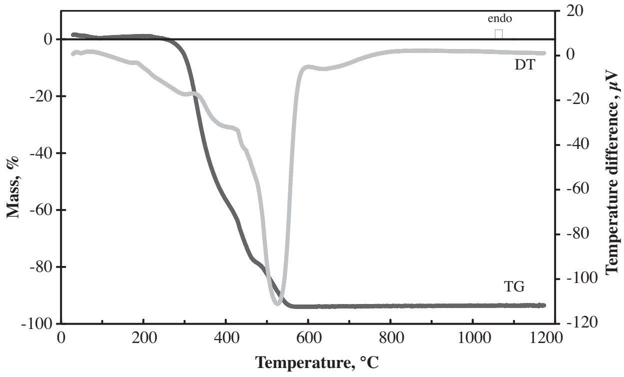

Fig. 12. TG and DTA results of PVA (KH 17).

Peaks for PVA were assigned based on Mansur et al. [39]. The major band between 3550 and 3200 cm^{-1} is assigned to the stretching of O—H bonds involved in the intermolecular and intra-molecular hydrogen bonds. The band between 2840 and 3000 cm^{-1} is assigned to the stretching of C—H bonds from alkyl groups. The band between 1750 and 1720 cm^{-1} is assigned to C=O and C—O bonds in the acetate group. The band in the region 1150–1085 cm^{-1} is assigned to C—O—C, and its relative intensity

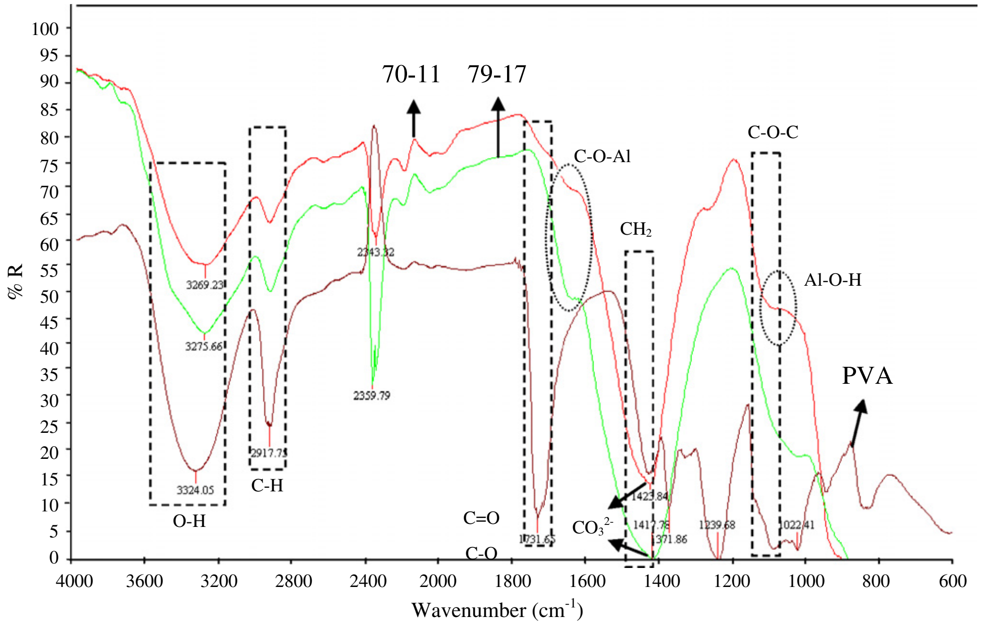

Fig. 11. FTIR spectra of MDF cements produced with two different cements (70% Al_2O_3 and 79% Al_2O_3) and PVA (KH 17).

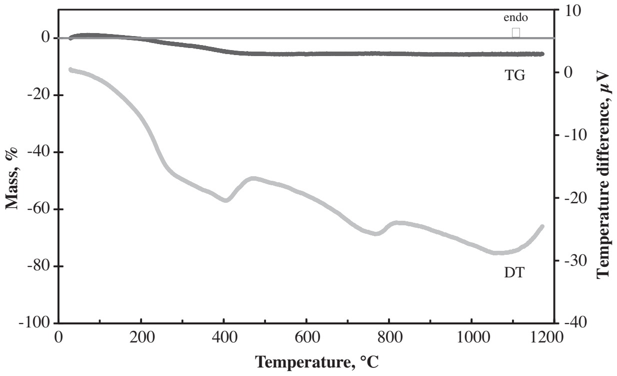

Fig. 13. TG and DTA results of 70-11.

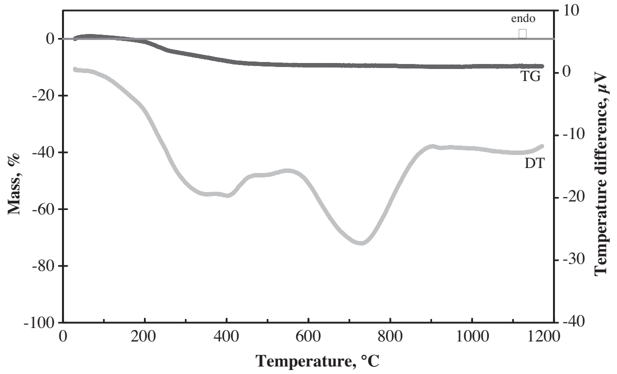

Fig. 14. TG and DTA results of 79-17.

indicates that the PVA is slightly crystalline. The band situated between 1461 and 1417 cm^{-1} is assigned to CH_2 groups.

The peaks from the spectra of 70-11 and 79-17 were assigned as follows. The band at 3270 cm^{-1} was assigned to O—H stretching in hydrates [40]. The band between 2840 and 3000 cm^{-1} is tentatively assigned to stretching of C—H bonds in the alkyl groups of the PVA, based on analysis of the PVA spectrum given above. The intensity of these two peaks is much smaller than the corresponding bands in the PVA. The band at 1630 cm^{-1}, seen in both MDF cement samples, can be assigned to a PVA-Al complex (vibration of C—O—Al), supporting the proposed mechanism of Desai [8] illustrated in Fig. 1. The intensity of this band is higher for 79-17 than for 70-11, reflecting the higher Al_2O_3 content of this cement. The weak band at 1090 cm^{-1} in 70-11 is probably due to Al—O—H bonds. The absorption band at 1020 cm^{-1} observed in 79-17 can be assigned to unreacted CAC phases (CA, CA_2, A) and the band at 1420 cm^{-1} can be attributed to the stretching vibration of CO_3^{-2} [40].

The bands observed in PVA at 1750 cm^{-1} (assigned to C═O bonds) and at 1239 cm^{-1} (assigned to the C—H bond) disappeared in both MDF cements. This fact suggests that the acetate groups were eliminated during the hydrolysis reaction.

The intensity (height) at 3324 cm^{-1} (due to OH groups) relative to the intensity at 2917 cm^{-1} (due to CH groups) was about 3.7 in the MDF cements and about 1.7 in the PVA. This difference is attributed to hydrolysis, which produces additional —OH groups in the MDF cement.

3.5. TG and DTA analyses

One PVA (KH 17 in Table 3) and two MDF cements, 70-11 and 79-17, were analyzed, all in powder form. The MDF cements were stored in a dry condition for 3 months until testing.

The PVA results are shown in Fig. 12. There are two small endothermic peaks at 190 °C and 320 °C. The first one has no mass change and is attributed to PVA melting [31]. Besides this, there are three major processes: an exotherm beginning at 230 °C that is attributed to dehydration, an exotherm beginning at 420 °C that is attributed to decomposition of acetate groups, and the strongest exotherm beginning at 470 °C and peaking at 526 °C, attributed to C—C chain breaking. The total mass loss was 96.2% [41–44].

The two MDF cements are shown in Figs. 13 and 14. The PVA decomposition is indicated by exothermic peaks and mass losses at temperatures from about 100 °C to about 400 °C, somewhat lower in temperature than in Fig. 12. The total mass losses were 9.3% for 70-11, and 13.0% for 79-17, reasonably attributed to loss of water and decomposition of PVA, given that the MDF cements contain approximately 6% PVA and around 9% water.

Figs. 13 and 14 show no evidence of carbonation, which has been reported in MDF cements after PVA degradation [15,22,45–48] and which was indicated in the FTIR spectra. If carbonates exist in the MDF cement they are expected to degrade around 800 °C by an endothermic process with mass loss. The exothermic transformation seen in Figs. 13 and 14 around 800 °C with no mass loss can only be attributed to some physical process such as re-crystallization or polymorphic transition and no such process is seen in the PVA. The carbonate bands observed in FTIR spectra at 1420 cm^{-1} in Fig. 11 can be explained by the time difference between the tests; the FTIR test was carried out 6 months after the

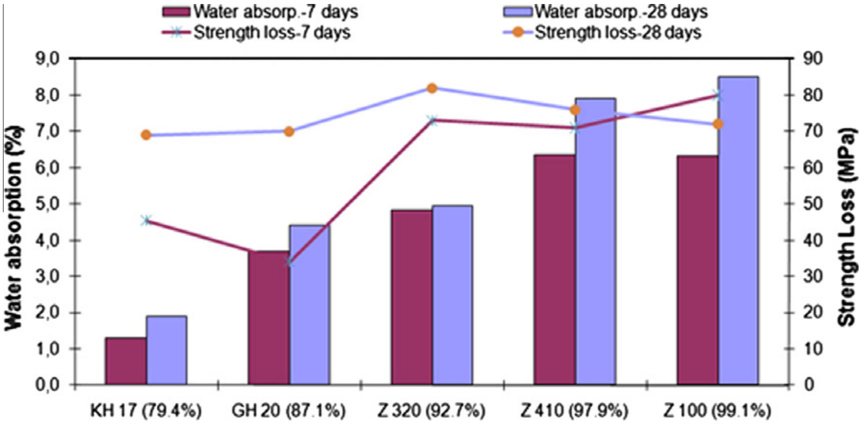

Fig. 15. Comparison of weight change with strength reduction (the numbers in parentheses in x-axis are hydrolysis degrees of PVAs).

thermal analysis, during which time reaction may have occurred with atmospheric CO_2.

The purpose of thermal analysis was to seek evidence of cross-linking in the MDF cement. No such evidence was found.

3.6. Water absorption

Water absorption of selected MDF cement specimens at 7 and 28 days is shown in Fig. 15 together with strength reductions of the water stored specimens. Higher water absorption has been used to indicate strength reduction [16]; however, Fig. 15 shows only a weak relationship between strength reduction and water absorption at 7 days and no relationship at 28 days.

4. Conclusions

- MDF cements were successfully produced with calcium aluminate cements whose alumina contents ranged from 42% to 79%. The most suitable cement contained 70% Al_2O_3. MDF cements were successfully produced with partially hydrolyzed PVAs whose degrees of hydrolysis were 80% and 87% and with acetoacetylated PVA. They were not successfully produced with fully hydrolyzed PVA, with carboxylated PVA, or with partially hydrolyzed PVA whose degree of hydrolysis was 73%.
- The highest biaxial flexural strength was about 260 MPa at 7 days and about 270 MPa at 28 days. This was obtained using cement with 70% Al_2O_3, w/c 0.11–0.15, and partially hydrolyzed PVA (80% and 87% DH).
- All specimens showed moisture sensitivity, indicated by a reduction in flexural strength on water storage. The specimens produced with different calcium aluminate cements showed reductions in strength between 15% and 83% after storing in water for 7 days and between 56% and 81% for 28 days. The specimens produced with different PVAs showed reductions in strength between 13% and 84% at 7 days and between 53% and 82% at 28 days. Reduction was smallest for MDF prepared with PVA whose hydrolysis degree was 80%, and was larger with PVAs whose hydrolysis degree was higher. The smallest reduction in strength was observed with alumina contents between 42% and 70%. Although, it seems possible to reduce the strength loss at 7 days due to water storage to a level as low as 15% by choosing optimum alumina content in cement and hydrolysis degree in PVA, the average strength reduction remained over 50% at 28 days even for those optimum cement and PVA compositions.
- The reduction in strength did not correlate especially well with water absorption.
- Preheating the polymer before mixing slightly increased the flexural strengths for the acetoacetylated PVAs.
- No cement hydration products were seen in XRD spectra of MDF cements confirming the results of other researchers.
- C—O—Al and Al—O—H bands, which can be evidence of cross-linking between cement and polymer, were observed in FTIR spectra of MDF cements.
- No evidence of carbonation after PVA degradation was observed in the TG-DTA results of MDF cements, contrary to the findings of other researchers and contrary to FTIR results.

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