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Macro-defect free cements
Influence of poly(vinyl alcohol), cement type, and silica fume

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Abstract

Macro-defect free cements were prepared using the following variables: processing (calendering and hand-mixing), poly(vinyl) alcohol (with different molecular weight and hydrolysis degree), cement (portland type I and slag-modified), and additions of silica fume. The results show that better processing is achieved by calendering the fresh paste and using poly(vinyl alcohol) with low hydrolysis degree and low molecular weight. Vickers hardness measurements indicate that materials prepared using portland type I cement are not significantly affected by humidity. Addition of silica fume lowers the acid resistance of these materials, suggesting that silica fume acts as an inert filler.

Keywords: Portland cement; Chemically bonded ceramics; Polymers; Characterization; Vickers hardness

Polymers have been extensively added to cementitious materials in order to improve some of their limitations, especially low-fracture strength and brittle behavior [1,2]. The most frequent ways to add polymers to cement-based materials are: (1) in bulk (the polymer is used as a solid); (2) dissolved in the water, (3) as a repair/impregnation material, and (4) as fibers [3–8]. The nature of polymer/cement interactions plays a major role in several properties of these composite materials, such as hydration [6], mechanical properties [9], and chemical resistance [10], among others.

One of the most promising cement-polymer composites was introduced by Birchall and colleagues [11]. This composite can be prepared using traditional polymer processing, such as calendering, extrusion, pressing, molding, etc., with a water/cement ratio lowered to 0.1–0.2, considerably lowering the overall porosity. Also, the flexural strength is about 150 MPa, while plain concrete shows values below 10 MPa [12]. The most frequently employed polymers are polyacrylamide, poly(vinyl alcohol) (PVA), and hydroxy methyl cellulose [13–15].

Since macro-defect free cements (MDFs) are prepared using water-soluble polymers, they show an important dependence between mechanical properties and humidity. In the first part of this study, a modification of Birchall's method was introduced in order to prepare MDFs [16]. In this new method, we suggested the use of a polymer (PVA) dissolved in water, while Birchall's method employs it in bulk. The total polymer content in our case is limited to the polymer solubility; the polymer content used was about 1% in relation to cement weight. Despite this low amount, the rheology of the fresh material allows the same polymer processing as described by Birchall. Another important modification was the use of a reticulating agent (sodium silicate) to limit the dependence between the humidity and mechanical properties.

Based on those initial results, it seems that the polymer acts mainly as a rheology modifier instead of a composite component. In fact, the volume fraction of the polymer, in relation to the whole material, is very low. It seems that by adjusting the rheological characteristics of the fresh paste, better materials can be obtained.

On the other hand, it is well known that many of the PVA properties are strongly influenced by molecular weight and hydrolysis degree. In this work, we studied the effects of the nature of PVA, cement, and silica fume addition upon the properties of the MDF obtained.

1. Methods

The following materials were used in this work: PVA, trade name Airvol, from Ipiranga Química (Sao Paulo/SP, Brazil); commercial sodium silicate (type H300 NDL) from Gessy Lever do Brasil (Sao Paulo/SP, Brazil); two different cements, slag-modified Portland cement, I (SM), trade name Ciminas (Ciminas S.A., Pedro Leopoldo/MG, Brazil) (the

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Table 1
Average molecular weight and hydrolysis degree of the PVA polymers and the designations adopted in this work*

Type	Hydrolysis degree (%)	Average molecular weight × 10^{-3} (kg · mol^{-1})	Designation
107	98–98.8	31–50	98-40
205	87–89	31–50	87-40
425	95.5–96.5	85–146	96-115
540	87–89	124–186	87-155

* Data provided by the manufacturer.

most employed cement in Brazil), and ordinary Portland cement—type I, trade name Vencemos, from Cemex S.A., Caracas, Venezuela. Silica fume was supplied by Elkem do Brasil, Rio de Janeiro/RJ, Brazil. The hydrolysis degrees and average molecular weights of the PVAs, as well as the designation adopted in this paper, are presented in Table 1.

PVA solutions were prepared by dissolving the polymer in water over a period of 24 hours; the maximum temperature used was 50°C. After complete dissolution, sodium silicate was slowly added, under stirring, for a period of about 4 hours. The resulting solutions were used immediately after preparation for replacing the water used for casting. The PVA and sodium silicate concentrations in the final solutions were always 5% (w/v) and 5% (v/v), respectively. Control specimen were prepared without any addition, using only water and cement. The specimens were processed in two different ways: (1) hand mixing followed by pressing—in this case, the polymer solution was added to the cement until a dough paste was obtained. This paste was transferred to the mould and pressed using a 2 MPa pressing pressure. (2) Calendering followed by pressing—same as described before, but using a calender in order to obtain the paste. The pressure was also 2 MPa. In addition, some of the test specimens were prepared in the same way as described previously, but part of the cement was replaced with silica fume.

Vickers hardness measurements were performed according to the Vickers printing method (ASTM E92-82). A hardness Vickers/Brinell measurer, Heckert-WPM model HPO 250 Heckert, Chemnitz, Germany, was used. Specimens were cured for 7 days at 50°C and 100% relative humidity. Later, the specimens were kept under two different conditions: wet conditioning (immersion in water for at least 4 h) and dry conditioning (specimens heated at 50°C for 24 h). Measurements were done using at least three different test specimens and the results represent an average of 10 single measurements.

Density was measured using a helium pycnometer, MicroMeritics model 65, Micromeritics, Norcross, USA. Measurements were performed after 7 days of curing.

Resistance to acid attack was performed on the samples cured for 7 days. The specimens were dried at 50°C until constant weight and immersed in HCl 5% (v/v) for 7 days. The samples were weighed at particular times and the weight loss was calculated. The HCl solution was replaced once a day.

2. Results and discussion

In the first part of this investigation the parameters necessary to qualify these materials as MDFs have been studied. In order to do so, the following variables were considered: the cement type, processing, and nature of PVA (average molecular weight and hydrolysis degree).

Table 2 shows the results of solution/cement ratio (s/c) obtained for cement pastes prepared by different processing, cement, and PVA types. These results indicate the minimum s/c ratio necessary to render pastes able to be processed. Single measurements are presented in Table 2.

As expected, calendering renders pastes with lower s/c ratios. This result is independent of the hydrolysis degree and molecular weight of PVA, as well as the cement used. Calendering is much more efficient than the hand-mixing process. Control specimens could not be obtained by calendering, since the fresh paste can not be processed.

Water/cement ratio values around 0.2 are characteristic for MDFs, and these are achieved using PVA with low hydrolysis degree (87%) independently of the molecular weight. For PVA with higher hydrolysis degree, MDFs were obtained only if the molecular weight was low. Both cement types tested provided MDFs but the best results were obtained using ordinary portland cement. Only one of the four PVA types (96-115) did not provide MDF, even by calendering.

Table 2
Minimum solution/cement ratio for pastes as a function of specimen processing, cement and PVA types*

		PVA type				
Specimen processing	Cement type	98-40	87-40	96-115	87-115	Control
Calendering followed by pressing	I (SM)	0.24	0.23	0.30	0.22	–
		0.25	0.25	0.33	0.27	–
		0.24	0.23	0.30	0.22	–
	I	–	0.23	–	0.23	
			0.19			–
Hand mixing followed by pressing	I (SM)	0.28	0.32	0.37	0.37	0.30
	I	–	–	–	0.29	0.25

* Control is the specimen without addition.

Table 3
Vickers hardness (MPa) of test specimens in dry and water saturated conditions*

		PVA type							
		98-40		87-40		87-155		Control	
Specimen processing	Cement type	dry	wet	dry	wet	dry	wet	dry	wet
Pressing after calendering	I (SM)	360 ± 60	290 ± 50	320 ± 20	290 ± 40	230 ± 90	220 ± 20		
						340 ± 90	220 ± 50	–	–
	I	–	–	370 ± 20	280 ± 10	250 ± 70	270 ± 20	–	–
					600 ± 90				
Pressing after hand mixing	I (SM)	90 ± 20	50 ± 10	100 ±10	60 ± 10	110 ± 10	70 ± 20	250 ± 20	160 ± 10
						160 ± 20	120 ± 30		
	I	–	–	–	–	280± 10	180 ± 10	–	–

* Each result represents an average of 10 measurements for at least three different test specimens.

Vickers hardness measurements were used to evaluate the dependence of MDFs with humidity. The results in Table 3 show that the humidity does not significantly affect Vickers hardness. When slag-modified cement was used, a slight dependence between hardness and humidity was observed. Processing also affects the hardness values. As a general trend, calendared specimens show a much higher Vickers hardness than hand-mixing samples. Also, the lower the s/c ratio, the higher the hardness measured. The highest hardness value found was 600 ± 90 MPa, referring to the specimen with the smallest solution/cement ratio (0.19).

For many materials, the Vickers hardness can be related to flexural strength, although this relation is not always so simple [17–19].

Based on these results, further experiments were made to characterize these MDFs, selecting the sample (87-40) with

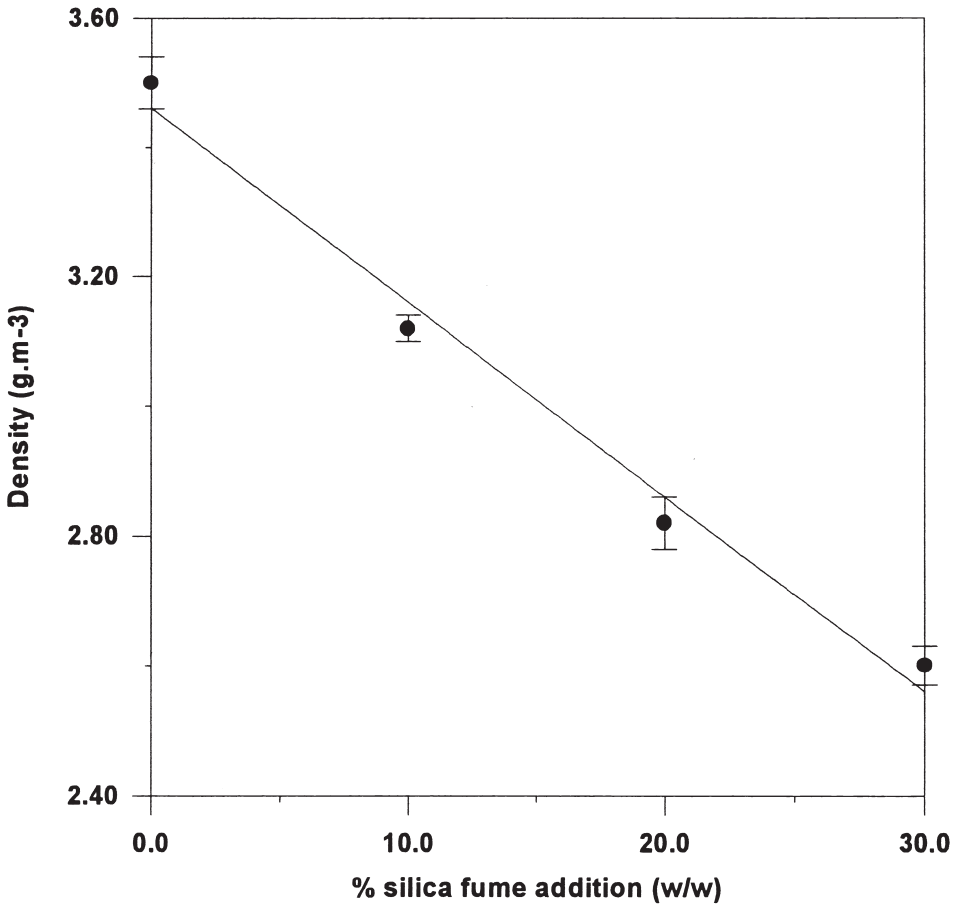

Fig. 1. Density of test specimen as a function of the silica content.

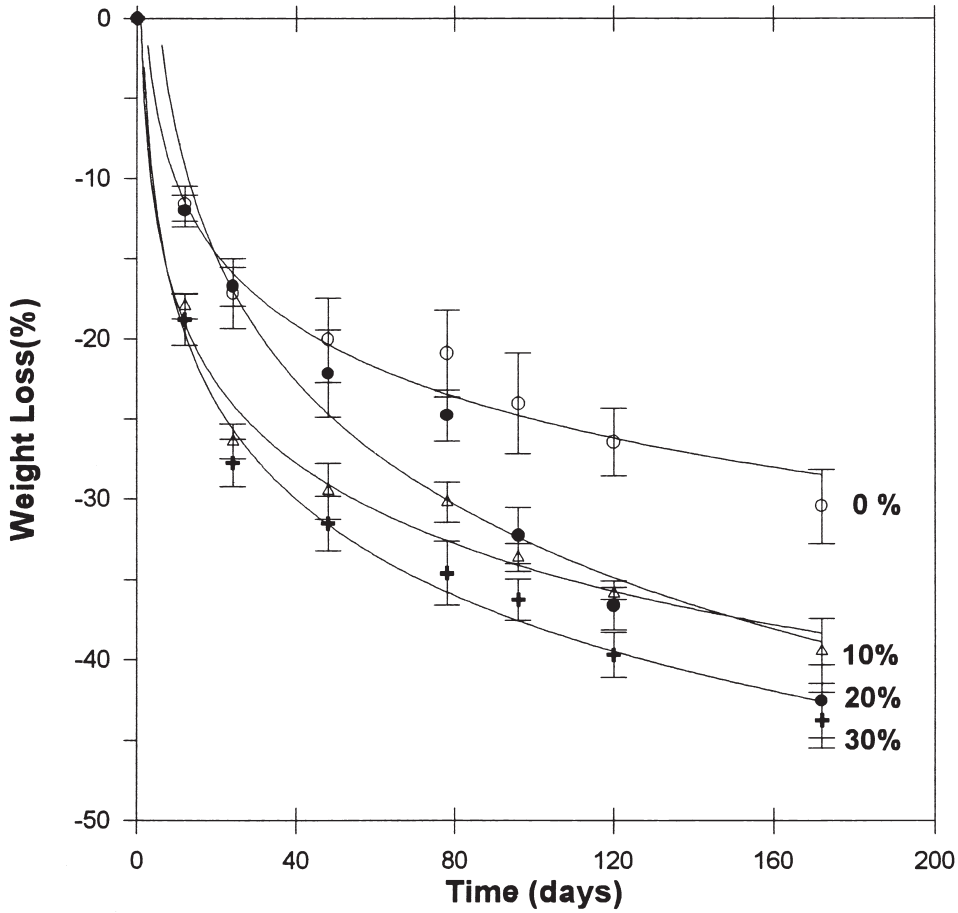

Fig. 2. Weight reduction of test specimen as a function of time. Test specimen was prepared with different amounts of silica fume and immersed in HCl 5% (v/v) solutions.

(s/c) ratio = 0.2. Silica fume was also added in order to evaluate the effects of this material. It is well known that silica fume enhances concrete properties, especially those related to porosity and strength [20,21]. Previous results [22] showed that the addition of silica fume to prepare MDFs does not require additional water, in relation to pastes prepared with only cement. This is a surprising observation, since in concrete technology the use of silica fume usually implies the use of a superplasticizer in order to obtain a good quality concrete [23]. Fig. 1 presents the density values of test specimens containing different amounts of silica fume.

Fig. 1 shows that the silica fume addition lowers the density almost linearly, which can be explained by the difference in the individuals densities (cement: 3.453 $g \cdot cm^{-3}$ and silica fume: 2.001 $g \cdot cm^{-3}$).

The effect of silica fume on the acid resistance was also investigated. The results are presented in Fig. 2 and show that the silica fume has a negative effect on the acid resistance. These results indicate that silica fume does not play the same role in MDFs as it does in conventional concrete. It is well known that silica fume in concrete reacts with $Ca(OH)_2$ produced from cement hydration, forming a calcium silicate. This material improves the resistance to acid attack. Also, it can fill the pore structure in concrete. Apparently, due to its very low porosity, the same process did not occur inside MDF. Probably the silica fume acts as an inert material, showing no reactivity under the conditions studied and thus showing adverse effect on the acid resistance.

3. Conclusions

It was shown that the characteristics of PVA play an important role in the rheological properties of MDF. The best results were obtained using PVA with low hydrolysis degree. Also, low molecular weight allows a better processing of the paste. Vickers hardness measurements indicated that these are not affected by water in a significant manner, probably due to low polymer content. The addition of silica fume has an adverse effect on this material, suggesting that under these conditions silica fume does not react with calcium hydroxide and works as an inert filler.

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