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MACRO-DEFECT FREE CEMENTS: A NEW APPROACH

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ABSTRACT

The in situ reticulation of the water-soluble polymer used to obtain macro-defect free cements is proposed as a way to minimize the shortening of the mechanical properties at high relative humidity. The polymer is used in solution, instead of in bulk. Data obtained with poly(vinyl alcohol) (PVA) and sodium silicate shows that PVA is insolubilized in the presence of this reticulation agent. In the presence of cement, the effect is enhanced. Micro hardness values obtained for bulk-PVA/cement and in situ reticulated specimens show that the reticulated specimens are not affected by humidity. Low w/c relations (0.2) and low polymer content (1%) are attainable. © *1998 Elsevier Science Ltd*

Introduction

Macro-Defect Free Cements (MDFs) are composites of a water-soluble polymer and a cement, characterized by its extremely low porosity and unusual mechanical properties. Flexural strength, for example, is at least one order of magnitude higher than that of plain concrete. The possible applications of these materials are extensive, varying from electronic substrate, armor ceramics, and substitution of fiber-reinforced plastics (1,2).

One of the most prominent features of these composites is the rheology of the fresh paste, that can be processed as polymers, using calendering, extrusion, molding, pressing, etc. A typical MDFs preparation method was developed by Birchall (3).

However, there are restrictions associated to these materials. Surely, the major limitation is the decay of mechanical properties at high relative humidities. This kind of problem is extensively reported in composite technology. (4–6) As explained by Fowkes, this behavior can be attributed to the relative intensities of the interactions between the components of the composite (7–9). When the composite is almost anhydrous, the interactions between the polymer and the cement matrix are due to van der Waals forces, a typical short range interaction. When molecules of water are put close together at the polymer-cement interface, van der Waals attraction is rather limited. In this case, water and polymer interact by an acid-base association, which is stronger than the original van der Waals force. The polymer

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interacts preferentially with water. In this sense, there is a competition between water molecules and cement matrix for the polymer.

To assure the appropriate rheological properties of the fresh paste, a water-soluble polymer is needed. In this sense, the presence of water will always reduce the polymer/cement matrix interaction. In order to limit this dependence there are many possible approaches, some of which are listed below:

1. *Reduction of polymer content*. This is the simpler approach that can be used, because as the polymer concentration is lowered, the effective polymer-cement interface is also reduced. On the other hand, Young (10) and Drábik (11), for example, pointed out that the micro chemical aspects of the interface in the polymer/cement matrix are of fundamental importance to the development of the mechanical properties of composite. Typically, the polymer content varies from 5 to 20%, in relation to cement weight. Using lower amounts of polymer, the mechanical properties of the composite could be negatively affected.
2. *Surface modification of polymer*. This approach has been used and showed good results, although is not extensively used at all, specially due to high costs involved (12).
3. *"In situ" reticulation of polymer*. This process could be controlled using a reticulation agent, but can result in changes, specially in the cement-polymer interaction, so an extensive chemical study is needed to control the overall properties of the composite.

We studied the third approach. First, the polymer reticulation is easier if the polymer is dissolved, so we used aqueous solutions instead of the solid polymer. Second, the reticulation agent must be inert with respect to the normal cement properties, so we used an inorganic, basic salt. In this work we show results obtained using a partially hydrolyzed poly(vinyl alcohol) (PVA) as the water-soluble polymer and sodium silicate solutions as the reticulation agent.

Experimental

Poly(vinyl alcohol) (PVA), Ipiranga Química, 87–89% nominal hydrolysis, was used without further purification. ASTM Portland Type I cement was used. Sodium silicate solutions H300 NDL were purchased from Gessy Lever do Brasil. These solutions have c.a. 25% SiO_2.

Films of pure and mixed PVA were obtained by casting, from aqueous solutions. The concentration of the PVA solutions varied from 1.0 to 5.0% w/v. In mixed films, sodium silicate solution from 0 to 5.0% v/v was added to aqueous PVA solutions. To prepare the mixed films containing cement, the cement was added to a freshly prepared solution of PVA/sodium silicate solution.

Films casted from PVA aqueous solution, from PVA/sodium silicate solutions, and from PVA/NaOH solutions were studied be Fourier-Transform infrared micro spectroscopy. The thickness of the films was c.a. 3 μm. The experiments were performed using a FT-IR spectrometer, Perkin-Elmer 16 PC, coupled to an Olympus microscope, that allows spatial resolution of about 1 mm^2. For the quantitative analysis, areas and intensities of IR bands were obtained through the equipment IRDM software. Normalization was carried out using the 2920 cm^{-1} area or intensity, because this IR band should be unaffected by both sodium silicate or NaOH, so being an appropriate internal reference.

In a first step, the homogeneity of the films was analyzed. Eight spectra of two individual films prepared from aqueous solutions of PVA 1% w/v with the addition of 1% v/v sodium silicate solution were obtained.

In a second step, a set of PVA films were obtained in two ways: 1) with additions of sodium silicate, and 2) with additions of NaOH. In both cases, the concentration of OH^- was varied from 10^{-4} to 10^{-1} $mol{\cdot}L^{-1}$.

The hydration rate of cement with and without sodium silicate admixture was studied using the gravimetric method (13). Flexural strength of plain and admixtured concrete was studied. Two series of test specimens were prepared: 1) an admixture free control, and 2) a batch with addition of sodium silicate, in which a solution of sodium silicate 2% v/v was used to prepare the concrete.

Water absorption and weight loss were performed following ASTM 570/63 gravimetric method. Circular films of 5.0 cm diameter and c.a. 30 μm thickness were casted from the appropriate aqueous solutions, and dried at 50°C in an oven until constant weight, being stored in a dissecator. The films were immersed in distilled/boiled water, at room temperature, for 24 h. The (non-solubilized) films were weighted. Finally, they were dried at 50°C until constant weight.

Micro hardness measurement were performed using a metalographic microscope Carl Zeiss VEB Metaval inverted incident Microscope provided with a micro hardness measuring accessory. Roughly describing, a diamond tip is pressed on the test specimen, engraving it; the area of the engraving is measured; the ratio between the applied force and the area engraved is the micro hardness value. Test specimens of two types were prepared. Fine PVA particles were added to cement at 1% w/w; water was added by calendering up to $w/c = 0.20$; the fresh paste was molded as plates 0.5 to 1.0 cm high and kept in an oven at 60°C and 100% relative humidity for 7 days. For the other type, cement was mixed in a calender with aqueous solution containing 5.0% w/v PVA and 5.0 v/v sodium silicate, up to $w/c = 0.20$; it follows that PVA/cement weight ratio is, again, 1%. The fresh paste was molded and aged as before. Both types of test specimens were polished prior to use. dry conditioning was attained by drying at 50°C for 24 h; wet conditioning was attained by immersion in water for at least 4 h.

Results

Initially, we studied the effect of the addition of sodium silicate solution on the properties of PVA, because sodium silicate is not described in the literature, to the best of our knowledge, as a reticulation agent. The most important feature is to have phase homogeneity, in the sense that an uniform distribution of both components in the solid state is achieved. This study was done using FTIR micro spectroscopy, because mixed films can be observed without any sample preparation, as would be the case for, say, electronic microscopy. A set of micro-FTIR spectra, obtained from different regions of a single film casted from PVA/sodium silicate aqueous solutions, is shown in Figure 1.

The FTIR spectra of pure PVA films and that of PVA/sodium silicate films show significant differences in the absorption bands at 1580 and 1720 cm^{-1}, only. For this reason, both bands were used in the IR study. The absorption band analysis is shown in Table 1.

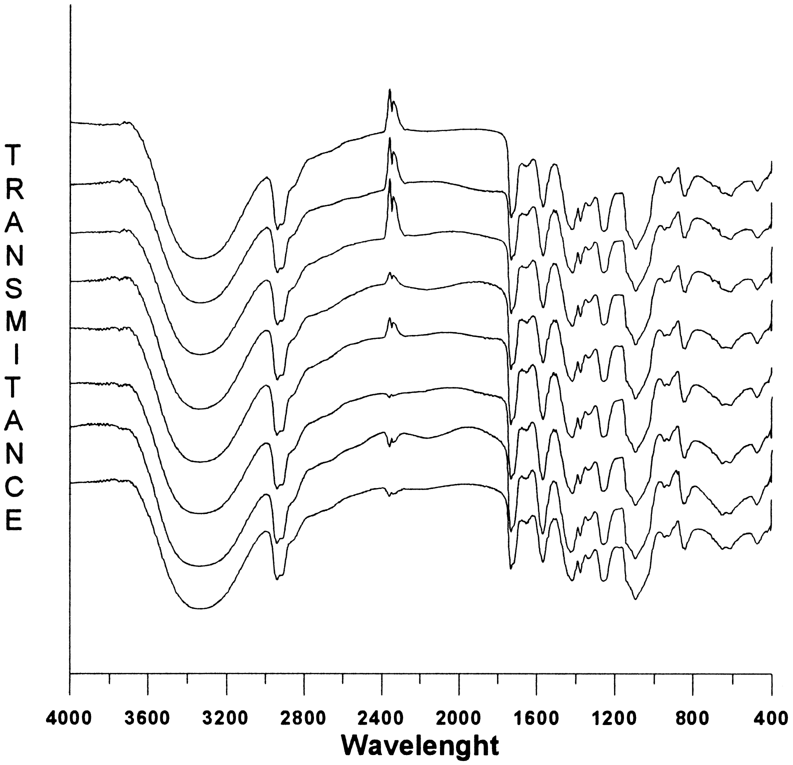

FIG. 1.
Infrared spectra of a film casted from an aqueous solution containing 1% w/v PVA and 1% v/v sodium silicate solution. Each spectrum was obtained from a different region of the same film. Each area corresponds to approximately 1 mm^2.

These results prove that the sodium silicate distribution in the PVA/sodium silicate films is uniform, at the resolution level of the technique.

The reticulation effect of sodium silicate was studied using PVA/sodium silicate films. Because PVA is high hydrophilic, a reduction in the weight increase after immersion in water means diminished hydrophilicity. Also, because PVA is soluble in water, the lower the weight lost after immersion in water and drying, the higher the reticulation. Table 2 shows results obtained varying PVA and sodium silicate concentration in the mother solution. The reticulation effect of sodium silicate is evident, because both, weight increase after immersion in water and weight loss after drying, are substantially reduced with the addition of sodium silicate.

The reticulation of PVA by sodium silicate in the presence of cement was studied casting mixed PVA/sodium silicate/cement films. Table 3 shows that in the presence of cement, the weight loss, that is, the non-reticulated amount of polymer, is further reduced. This result is straightforward in pointing that the “in situ” reticulation of PVA by sodium silicate in cement materials is achievable.

However, the chemical nature of the reticulation process needs further study. We studied the effect of the basicity of the mother solutions onto reticulation. Because the PVA assayed

TABLE 1
Comparison of the uniformity of sodium silicate distribution in two films casted from aqueous solutions of 1% w/v PVA plus 1% v/v sodium silicate. Data refers to the average area ratio and average intensity ratio of bands at 1720 and 1580 cm^{-1} using the 2920 cm^{-1} band as reference. Data from 10 micro FTIR spectra on each film.

	Ratio of Areas		Ratio of Intensities	
Film	(1720/2920)	(1580/2920)	(1720/2920)	(1580/2920)
1	0.46 ± 0.01	0.37 ± 0.05	0.75 ± 0.03	0.58 ± 0.06
2	0.44 ± 0.02	0.28 ± 0.05	0.67 ± 0.10	0.47 ± 0.10

is only partially hydrolyzed, the degree of hydrolysis increases in basic solution. Sodium hydroxide, having an inert cation, was used to cast mixed PVA/NaOH films. These films are water soluble in any composition, showing no reticulation effect. A quantitative FTIR study of band absorption at 1580 cm^{-1} and 1720 cm^{-1} was carried out, for comparison between both inorganic substances. Figure 2 shows that the effect of the addition of NaOH is similar to the addition of sodium silicate, with regard to IR spectroscopy. The number of carbonyl groups increases slightly more in the presence of NaOH, and the number of salt groups increases less. The results prove that the “in situ” hydrolysis has no reticulation effect.

The effect of admixing sodium silicate to cement with regard to flexural strength and

TABLE 2
Effect of sodium silicate onto PVA properties. Films casted from aqueous solutions of PVA and sodium silicate, in the concentrations listed. Weight increase of each film as obtained after 24 h immersion in water. Weight loss after drying the immersed films.

PVA (% w/v)	sodium silicate (% v/v)	weight increase after immersion (%)	weight loss after drying (%)
1.0	0	soluble	100
	0.5	soluble	100
	1.0	223 ± 12	34.2 ± 5.1
	2.0	34.5 ± 15.5	14.1 ± 3.7
2.0	0	soluble	100
	1.0	242 ± 27	36.9 ± 3.7
	2.0	126 ± 26	15.3 ± 4.2
4.0	0	soluble	100
	1.0	soluble	100
	4.0	53.5	10.2 ± 0.9
5.0	0	soluble	100
	5.0	40.0 ± 4.1	2.4 ± 1.9

TABLE 3
Effect of sodium silicate onto mixed PVA/cement properties. Films casted from aqueous solutions containing 5% w/v cement and PVA and sodium silicate, in the concentrations listed. Weight increase of each film as obtained after 24 h immersion in water. Weight loss after drying the immersed films.

PVA (% w/v)	sodium silicate (%, v/v)	weight increase (%)	weight loss after drying (%)
1.0	0	310 ± 21	27.1 ± 11
	0.5	270 ± 14	26.0 ± 7.2
	1.0	114 ± 13	10.2 ± 3.1
	2.0	29 ± 3.1	6.7 ± 1.9
2.0	0	294 ± 19	23 ± 10
	1.0	267 ± 19	9.2 ± 2.7
	2.0	81.0 ± 3.1	8.2 ± 4.1
4.0	0	315 ± 18	27.2 ± 12
	1.0	295 ± 27	27.2 ± 13
	4.0	50.7 ± 8.2	5.1 ± 3.9
5.0	0	320 ± 11	27.2 ± 9.9
	5.0	20.1 ± 3.7	2.7 ± 2.5

hydration rate was studied. Table 4 and Figure 3 show that sodium silicate has no significant effect on both parameters, allowing its use as a reticulation agent in cement based materials.

Finally, we casted test specimens of PVA/sodium silicate/cement in order to compare their micro hardness with ordinary bulk PVA/cement specimens, at low and high relative humidity. The results are shown in Table 5.

Discussion

A number of PVA reticulating species is described in the literature, as boric acid, vanadates, corants, copper salts, etc. In a general reticulation process, two steps are involved: the attachment of the reticulating agent to an individual chain of PVA and, then, the join to another chain (14–17). In sodium silicate solutions, there are many chemical species, the most important being: colloidal silica, $Si(OH)_4$ and $HSiO_3^-$. According to Iler (18), when a sodium silicate solution is diluted, there is an increase in particle size, increasing the acidity of the species grown. Colloidal silica shows a pKa varying from 6.8 to 7.1; $Si(OH)_4$ shows a pKa of 10.6. Boric acid, a commonly used reticulation agent, has a pKa = 9.2 (19–21).

On the other hand, using the concepts of hard and soft bases and acids, as the silicate chains grow, the hardness of these species becomes higher. So, it can be predicted that sodium silicate will reticulate PVA. The reticulation is probably based in two ways:

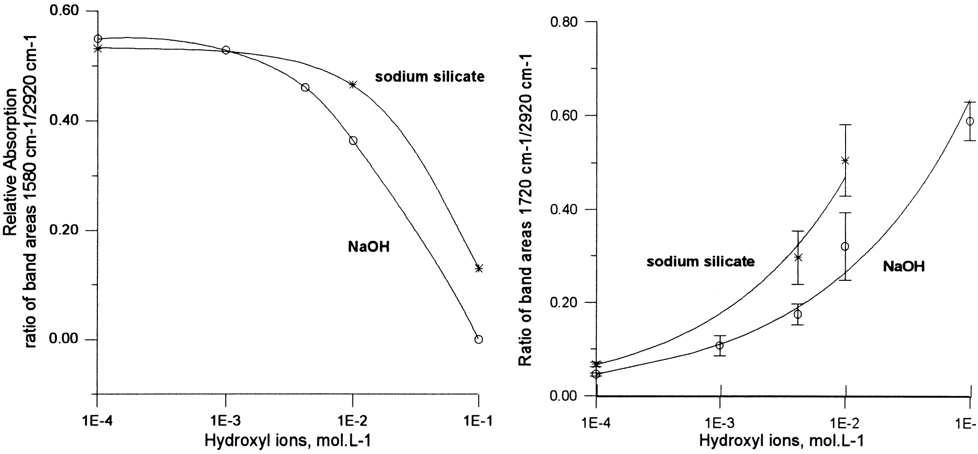

FIG. 2.

Comparison of the effect of the addition of sodium silicate and NaOH on PVA FTIR spectra, as a function of the nominal concentration of hydroxyl ions. The areas of the absorption bands at 1580 and 1720 cm^{-1} were normalized using the area of the absorption band at 2920 cmK−1. Films casted from aqueous solutions containing 1% w/v PVA and the appropriate concentration of sodium silicate or NaOH.

1. Complexation of PVA hydroxyls groups by sodium silicate species; this mechanism is not visible in infrared spectra due to the great number of hydroxyls present in the system.
2. Complexation of some hydrolysis products of PVA, due to the basicity of the solutions, by sodium silicate, that in principle, are associated to absorption bands at 1580 cm^{-1} and 1720 cm^{-1}.

Indeed, the presence of other ions in cement could enhance the reticulation, but a more detailed study is needed.

Micro hardness is a property seldom used in cement and concrete technology, although frequent in other areas. The literature points that micro hardness can be related to mechanical properties, especially to flexural strength. In metallic materials, this correlation is easier than in ceramics (22–24). So, we used this kind of measurement to study the dependence between

TABLE 4

Flexural strength of cement test specimens as a function of age. Control: cement and water; Admixtured: cement and aqueous solution of sodium silicate 2% v/v. In both cases w/c = 0.45 and duplicates.

	Flexural Strength (MPa)	
Test Specimen	7 days age	28 days age
Control	4.4 ± 0.2	5.7 ± 0.1
Admixtured	4.4 ± 0.1	5.6 ± 0.2

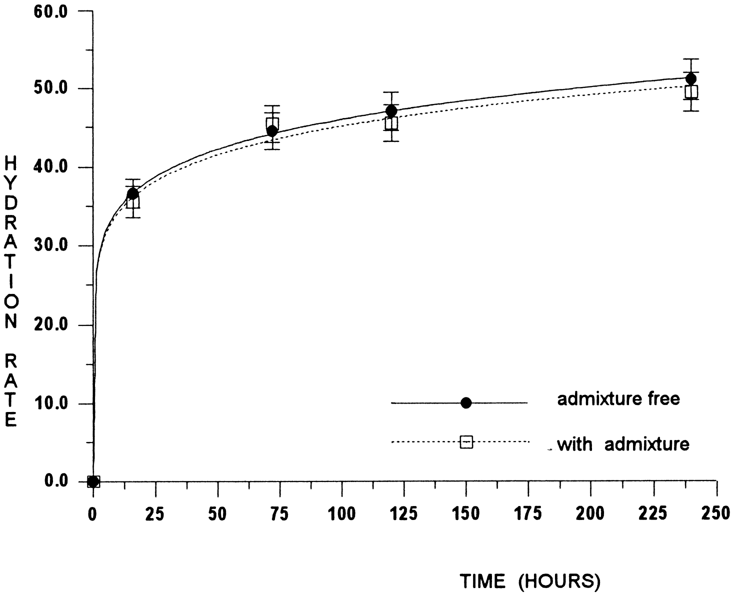

FIG. 3.
Cement hydration rate for control test specimens (cement and water) and for text specimen with admixture (cement and aqueous solutions of sodium silicate 1% (v/v)). In both cases, w/c = 3.

relative humidity and mechanical properties, in a comparative way. The results, reported in Table 5, show that the materials prepared as described in this work are not affected by relative humidity. In fact, it was possible to prepare materials containing only 1% of PVA, in relation to cement mass, using a w/c ratio of 2.

TABLE 5
Micro hardness of test specimens in dry and water saturated condition. Bulk PVA: test specimens prepared by mixing 1% w/v solid PVA to cement and w/c = 0.20. In situ reticulated PVA: test specimens prepared by mixing cement with an aqueous solution containing 5% w/v PVA and 5% v/v sodium silicate solution, instead of water, at w/c = 0.20. Age of 7 days. At least ten measurements in each case.

	Micro hardness (MPa)	
Test specimens	Dry	Wet
Bulk PVA	175 ± 20	100 ± 9
In situ reticulated PVA	460 ± 30	410 ± 20

Conclusions

The overall results reported in this work show that the approach tested is really promising. The “in situ” reticulation can be achieved and the hydrophilicity of PVA is reduced. Indeed, the amount of PVA needed in order to obtain MDFs is only 1% in relation to cement weight, without loss of rheology of the paste. The micro hardness of test specimens so prepared make believe that the dependence between high relative humidity and mechanical properties can be eliminated.

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