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Polymer-modified cement using belite-rich cement and carbonation reaction

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HIGHLIGHTS

- At 10% dosage, 64.6% of EVA remained in liquid and 35.4% was adsorbed on cement.
- Carbonated polymer-modified belite-rich cement has high bending strength.
- EVA addition increased reactivity of carbonated belite-rich cement.
- EVA addition decreased pore volumes of carbonated samples.

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ABSTRACT

This paper describes the hardening mechanisms and mechanical properties of a new polymer-modified cement (PMC), produced by carbonation of belite-rich cement. A PMC containing carbonated belite-rich cement and ethylene vinyl acetate (EVA) copolymer has high bending strength, and carbonation improves the toughness. The reaction rate of the cement is related to the amounts of CO_2 in carbonated samples with or without EVA. The reaction of belite is accelerated by carbonation and the addition of EVA. The pore volumes of carbonated samples containing EVA are smaller than those of EVA-free samples.

1. Introduction

Shell is an interesting composite material [1,2]. Shell consists of 95% calcium carbonate and 5% protein, and has good mechanical properties and durability. It has been reported that penetration of concrete by Cl^- was prevented by adhesion of barnacles on the concrete surface as a result of an adhesion layer composed of calcium carbonate and protein [3]. Combinations of calcium carbonate and polymers could provide useful new materials.

CO_2 emissions by the cement industry need to be reduced. Carbonation reactions for CO_2 fixation, and the strengths of various carbonated cements have been studied. Carbonated belite-rich cement (LHC: low-heat Portland cement) has high strength [4]. Half of the CO_2 generated during LHC production can be fixed by carbonation. Watanabe et al. reported highly durable carbonated cementitious materials containing belite-rich cement and γ-C_2S as the main components [5]. In particular, carbonated highly durable concrete has long-term resistance to Ca leaching of hardened concrete. This material is expected to be used for radioactive waste disposal facilities.

Polymer modification of cements improves the adhesion, flexural strength, and crack resistance of the cement. Because of these superior properties, polymer-modified cements (PMCs) have been used as tile adhesives, finishing materials, and repair materials. The mechanical strength of the cement is improved by polymer film formation [6,7] and dispersion of soft polymer particles in the cement. In our previous report, we suggested that the bending strength and crack resistance of a PMC was increased by the action of soft polymer particles in the hardened body, and the adhesive strength was improved by the formation of polymer films [8]. Polymer particle dispersion and polymer film formation are both useful composite mechanisms in PMCs. The development of new cementitious system materials with excellent strength and durability

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could be achieved using a combination of carbonation of the cement hardening body and a polymer cement, similar to shell. In this study, we investigated the carbonation reaction and mechanical properties of hardened belite-rich cement with added ethylene vinyl acetate (EVA) copolymer to develop new environmentally friendly composites and repair materials.

2. Experimental

2.1. Materials

The chemical and mineral compositions of belite-rich cement (LHC, Taiheiyo Cement Co., Ltd.) are shown in Tables 1 and 2. The density of LHC is 3.22 g/cm^3. EVA was obtained from the Denka Co., Ltd.; its properties are shown in Table 3. The average particle diameter of EVA was 0.6 μm and the density was 1.06 g/cm^3. Table 4 shows the mixing proportions of cement paste and mortar, with or without polymer dispersion.

Specimens of dimensions 20 × 20 × 80 mm were prepared. The reaction was analyzed using paste samples, and mortar samples were used for investigation of the mechanical properties. The EVA dosage was 10 mass% of polymer with respect to cement. The water to cement ratio was 0.5 or 0.4, without or with EVA, respectively. The cement to sand ratio in the mortar was 1:2. Pastes were mixed using a hand mixer and mortars were mixed for 5 min using a mortar mixer (JIS R 5201). The paste was remixed after 2 h and formed in a mold to prevent paste bleeding.

EVA-free samples were cured in water for 6, 13, and 27 d after curing under wet conditions for 1 d. The PMC was cured under wet conditions (relative humidity 60%) at 20 °C. The samples were also cured in an accelerated carbonation chamber for 7, 14, and 24 d, according to JIS A 1153 (“Method of accelerated carbonation test for concrete”), after curing under wet conditions for 7 d. Accelerated carbonation was performed at 20 °C, 60% relative humidity, and 10% CO_2. The curing times were 14, 21, and 35 d.

2.2. Polymer adsorption

Samples were mixed for 1, 5, and 10 min at 20 °C. The amount of polymer adsorbed on the cement was calculated from the polymer concentrations in the initial solution and in the liquid phase (after polymer adsorption), which was obtained by centrifugal separation (3000 rpm) of the cement paste containing the polymer dispersion. The unadsorbed polymer concentration was measured using a total organic carbon analyzer (TOC). TOC measurements performed on the cement paste at 1, 5, and 10 min after initial mixing showed that adsorption equilibrium was achieved within 1 min. In this study, a 5-min adsorption time was used to ensure equilibrium conditions.

2.3. Reaction analysis

The reaction of a paste sample was stopped after a prescribed time using a large amount of acetone; the product was dried for 16 h at 40 °C. The amounts of unreacted alite and belite were determined by quantitative X-ray diffraction (XRD) using 10 mass% α-alumina as an internal standard. The reaction rates of alite and belite were determined by correction for ignition losses from the hardened samples. The sample ignition losses were determined using differential thermal analysis-thermogravimetry from the mass loss at 1000 °C. The pore volumes of the hardened samples were determined using the Archimedes method. The inorganic carbon content of the carbonated sample was determined using a total organic carbon meter with a solid-sample fuel system, and the amount of adsorbed CO_2 was calculated. The amount of CO_2 adsorbed on LHC was calculated from the ignition loss of the carbonated cement.

2.4. Investigation of mechanical properties

The mortar bending strength was measured using a three-point bending test based on JIS R5201. The strain was measured by placing a strain gauge on the test specimen.

3. Results and discussion

Table 5 shows the results for EVA adsorption. The amount of polymer adsorbed on the cement was calculated from the residual amount of polymer in the liquid phase and the initial polymer concentration. When 10 mass% of polymer was added to the cement, the polymer concentration in water [$(P/(P+W)$; P: polymer, W: water] was 20 mass%. The concentration of residual polymer in the liquid phase was 12.9 mass%. Rottstegge et al. suggested that a polymer adsorbed on an inorganic material acts as a glue [9]. Adsorbed and non-adsorbed polymer both improve the PMC performance. When the polymer dosage was 10 mass%, 64.6% of the EVA remained in the liquid phase and 35.4% was adsorbed on the cement. After PMC hardening, the particles that remain in the liquid phase form hydrates.

Fig. 1 shows the bending strengths of carbonated and hydrated mortars with or without EVA. Carbonation significantly increased the bending strengths of the hardened samples, regardless of the presence of EVA. The bending strength of the carbonated sample

Table 1
Chemical composition of LHC.

Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	R_2O	Total
0.9	26.1	2.9	2.3	63.9	0.8	2.3	0.1	0.4	99.7

Table 2
Mineral composition of LHC.

Kind of cement	Mineral composition (mass%)					
	f-CaO	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
LHC	0.1	32.3	50.6	3.74	6.96	3.84

Table 3
Polymer dispersion properties.

Items	Contents
Kind of polymer	Ethylene vinyl acetate copolymer
Polymer content (mass%)	46.4
Emulsifier	Poly(vinyl alcohol)
Tg (°C)	1
pH	4.8

Table 4
Mix proportions of paste and mortar.

	Cement	Water	Polymer
Plain	100	50	0
PMC	100	40	10

(Polymer: Polymer content).
Mortar: Ratio of sand to cement is 2.0.

Table 5
EVA adsorption on cement.

Adsorption of EVA	Residual concentration of EVA in liquid phase
30.4 mg/g	12.92 mass%

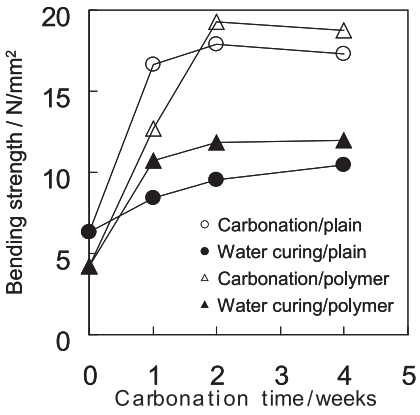

Fig. 1. Mortar bending strengths.