

New Polymer-modified Cement Using Belite-rich Cement and the Carbonation Reaction

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1. Introduction

Organic shell material is a very interesting composite from the perspective of materials science [1,2]. Shell consists of 95% calcium carbonate and 5% protein, and is an excellent composite in terms of mechanical properties and durability. Authors have previously reported that the penetration of Cl^- into concrete is prevented by the adhesion of barnacles onto the concrete surface, and that this is the effect of the adhesion layer of the barnacle, composed of calcium carbonate and protein [3].

The cement industry is under pressure to reduce the amount of emitted CO_2 . Previous studies have already examined the carbonation reaction and the strength of various cements from the viewpoint of CO_2 fixation and the high strength of carbonated belite-rich cement (LHC: low-heat Portland cement) [4]. Half of the CO_2 generated in the production of LHC can be fixed by the carbonation reaction.

Polymer-modified cement (PMC) is used to improve the adhesion, flexural strength, and crack resistibility of cement. Given these superior properties, PMC has been used as an adhesive for tiles, finishing materials, and repair materials. It is thought that mechanical strength is improved when using the polymer because of film formation [5] and the effect of dispersed soft polymer particles within the cement. In our previous report, we suggested that the bending strength and crack resistibility of PMC is enhanced by the action of soft polymer particles in the hardened body, and that the adhesive strength of PMC is improved by the formation of polymer films [6]. Both the dispersion of polymer particles and the formation of polymer films are useful composite mechanisms for PMC.

The development of a new and superior cementitious system material, in terms of strength and durability, is expected from the combination of the carbonation reaction of the above-mentioned cement hardening body with polymer cement that is similar to shell material. This paper discusses the carbonation reaction and the mechanical properties of hardened belite-rich cement with ethylene vinyl acetate polymer emulsion (EVA) to produce a new and environmentally friendly composite material.

2. Experimental

2.1 Materials and specimens

The chemical and mineral composition of belite-rich cement (LHC, Taiheiyo Cement Co., Ltd.) is shown in Tables 1 and 2. Chemical composition of LHC was analyzed by JIS R 5202 "Chemical analysis for portland cement". The mineral composition of LHC was calculated by Bogue formulas. The polymer emulsion used in this study is EVA (Dispersing agent: Poly (vinyl) alcohol, Denki Kagaku Kogyo Co., Ltd.).

Table 1 Chemical composition of LHC

lg.loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	R ₂ O
0.87	26.12	2.87	2.29	63.9	0.75	2.26	0.12	0.40

Table 2 Mineral composition of LHC

f-CaO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄
0.1	32.2	50.6	3.74	6.96	3.84

Specimens were prepared at a size of 20×20×80 mm. Paste samples were used for analysis of the reaction, while mortar samples were used for the measurement of mechanical properties. The dosage of EVA to the cement is 10 mass%. The water-to-cement ratio is 0.5 without EVA polymer and 0.4 with polymer. The cement-to-sand ratio in the mortar is 1:2. Sand was ISO standard sand. Samples were cured in water for 7 days and then cured in wet conditions for 1 day. Samples were then cured in RH60% and a CO₂ concentration of 10%. For comparison, standard curing samples were cured in following conditions: plain samples without EVA were cured in water, and polymer samples with EVA were cured in RH60% at 20°C.

2.2 Analysis of the reaction

The reaction of paste samples that were set to react for a prescribed time was stopped using a large amount of acetone; samples were then dried for 16 hr at 40°C. The amounts of unreacted alite and belite were determined by X-ray diffraction (XRD). XRD peak area were obtained by numerically integrating function fitting the peak profile obtained by XRD. α -Al₂O₃ was used as internal standard at 10mass%. The ignition loss of samples was obtained from the amount lost at 1000°C by DTA-TG. The pore volume of hardened samples was measured using the Archimedes method. The amount of inorganic carbon within the carbonated sample was measured using a total organic carbon meter with a solid sample fuel system, from which the amount of CO₂ absorption was then calculated.

2.3 Measurement of mechanical properties

The bending strength of the mortar was measured using the three-point bending test, based on JIS R5201. Simultaneously, the amount of strain was measured by attaching a strain gauge to the test specimen.

3. Results and discussion

Figure 1 shows the bending strength of carbonated and hydrated mortars with and without EVA. The bending strength of hardened samples increased markedly with carbonation, regardless of the presence of EVA polymer. The bending strength of the carbonated sample with EVA is lower than that of the sample without EVA at early stages; however, at later stages, the opposite result is obtained.

Figure 2 shows the stress–strain curves of hardened samples with and without EVA polymer. The addition of EVA led to an improvement in the toughness of hardened samples and an increase in bending strength. This trend is most pronounced in the carbonated sample.

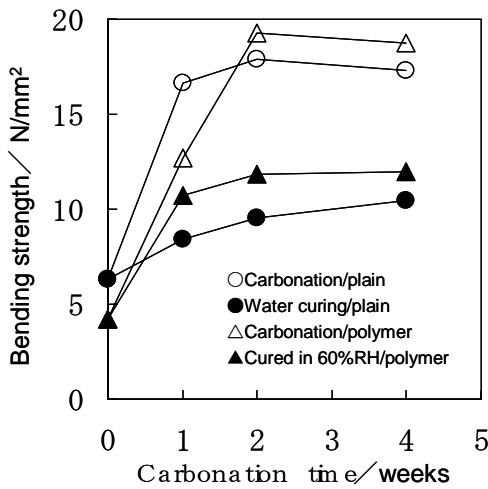


Fig.1 Bending strength of hardened samples

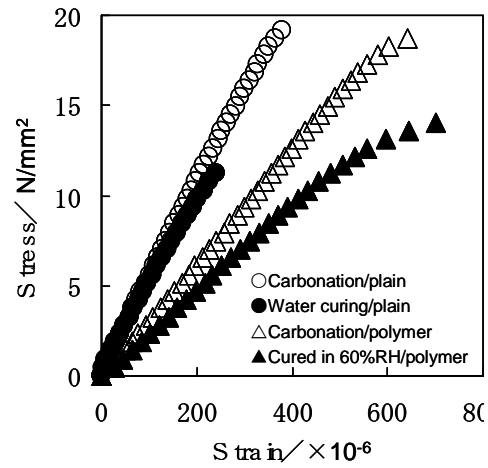


Fig.2 Stress-strain curves of hardened samples

Figure 3 shows the degree of reaction of alite and belite in carbonated samples. In previous report, it has been reported that the reaction of LHC without EVA was accelerated by carbonation condition compared with the case of water curing condition [4].

In pre-cured samples, the degree of reaction of alite for samples with EVA is lower than that for plain samples. The reaction of alite was delayed by adding EVA after 7 days of pre-curing. When samples were cured for 28 days after pre-curing, the degree of reaction of alite with and without EVA polymer was the

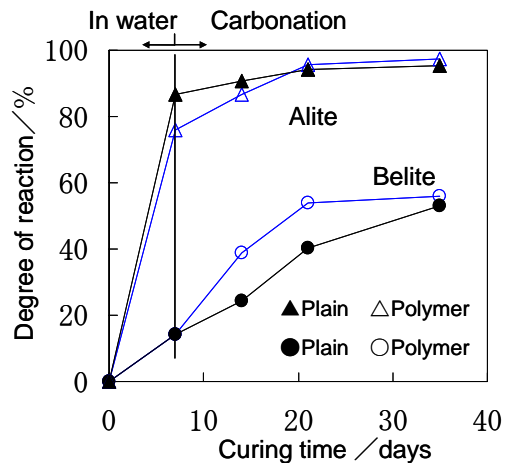


Fig.3 The degree of reaction of alite and belite in carbonated samples with or without EVA

same. The reaction is accelerated by carbonation.

The degree of reaction of belite for samples with and without EVA polymer is similar for different pre-curing intervals. The reaction of belite is accelerated by carbonation at early stage. The degree of reaction of belite for carbonated samples with EVA polymer at curing time from 14 days to 21 days is greater than that for samples without EVA polymer; however, the degree of reaction of belite for plain samples increases at late stages of the process. For samples that were carbonation-cured for 28 days, the degree of reaction of belite is similar for samples with and without EVA.

In carbonated samples, calcite and vaterite were detected using XRD. The gel phase is produced from carbonated C-S-H. In a previous paper, the composition of the gel phase was estimated to be $0.77\text{CaO} \cdot \text{SiO}_2 \cdot 0.04\text{Al}_2\text{O}_3 \cdot 0.15\text{CO}_3 \cdot 2.18\text{H}_2\text{O}$ for carbonated samples [4].

The CO_2 absorption capabilities of carbonated samples are shown in Fig. 4. With the addition of EVA, CO_2 is commonly absorbed from an early stage, and the amount of CO_2 absorption indicates a large value for plain samples at late stages in the process. The amount of CO_2 absorption for plain samples is only minor at early stages, but it increases markedly thereafter. It has been reported previously that the degree of reaction of belite is accelerated by carbonation [4]. The addition of EVA polymer acts to increase the amount of CO_2 and accelerate the reaction of belite within the carbonated sample.

Figure 5 shows the relation between the amount of CO_2 absorption and the degree of reaction of belite and alite for carbonated samples. A linear relationship is apparent, regardless of EVA addition. In general, the hydration reaction is delayed by adding EVA; however, we clarified that the

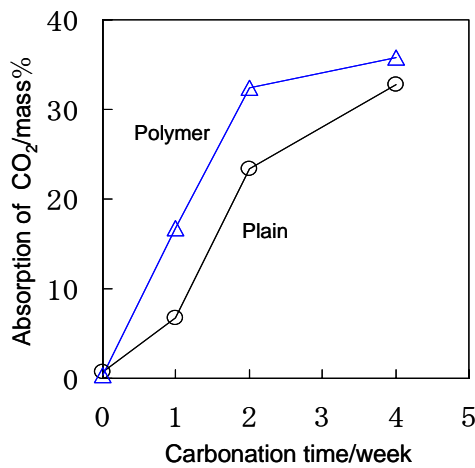


Fig. 4 CO_2 absorption on carbonated samples with or without EVA.

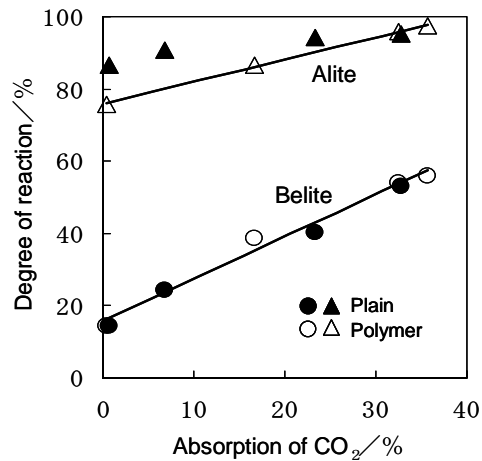


Fig.5 Relation between the degree of reaction and CO_2 absorption

delay effect of EVA-addition is almost negligible when comparing the acceleration of the reaction by carbonation (Fig. 5). The addition of EVA promotes the carbonation reaction, leading to an increase in the degree of belite reaction. It is presumed that polymer particles are made nucleus of CaCO_3 formation and it becomes easy to formation of CaCO_3 . More detail investigations are necessary for acceleration mechanisms of polymer addition.

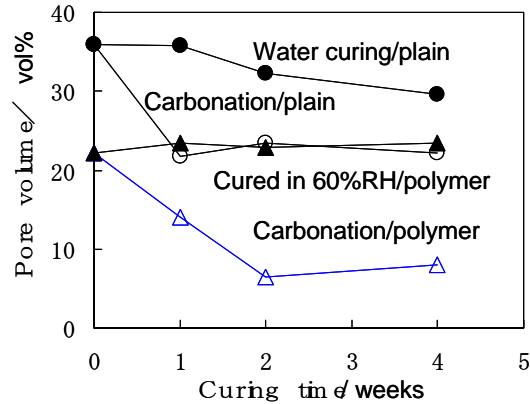


Fig.6 Pore volume of hardened samples

The rate of carbonation of hardened cement is closely linked to the microstructure of the hardening body. Carbonation is readily advanced if a large number of pores define the diffusion path of CO_2 . Figure 6 shows the pore volume of hardened samples with and without EVA, as measured using the Archimedes method. The pore volume of hardened samples with EVA is smaller than that of plain samples. This finding reflects the filling of polymer particles, the formation of a polymer film, and the water-reducing effect of the EVA emulsion polymer. The water-to-cement ratio of plain samples is 0.5, and this is reduced to 0.4 by adding EVA polymer at constant fluidity.

We have already reported that pores are filled by the carbonation reaction of the LHC hardening body [4]. The pore volume of carbonated samples with EVA decreases, as with that for plain samples. Moreover, the addition of EVA leads to a greater reduction in the pore volume of hardened samples than for plain samples.

It appears that densification of the microstructure by carbonation is positively advanced with the addition of EVA polymer. Thus, the pore volume of samples hardened with polymer is less than that of plain samples. The difference in the degree of CO_2 absorption for hardened samples with and without EVA polymer cannot be described from pore volume alone. It is necessary to consider why the amount of CO_2 absorption is large even though the microstructure is dense in the case of samples with EVA polymer. We speculate that the addition of polymer influences humidity within the hardening body and consequently the nucleation of calcium carbonate. Previous studies have considered the relation between the water-to-cement ratio, atmospheric humidity, and the carbonation reaction, and found that a moderate volume of water is

necessary for progress of the carbonation reaction [7]. That is, the carbonation reaction doesn't progress under conditions of extreme drying and high humidity. It is thought that the addition of EVA led to the situation that the interior of the hardening body was maintained at a level of humidity appropriate for carbonation. It is also possible that Ca^{2+} adsorbs the EVA emulsion grain, thereby facilitating the nucleation of calcium carbonate. In terms of nucleation, Silva and Monteiro suggested that EVA particles appear to act as sites of C-S-H nucleation from solution [8]. Additional detailed investigations are necessary to understand these mechanisms.

4. Conclusions

This paper describes the hardening mechanisms and mechanical properties of polymer-modified cement (PMC) using the carbonation reaction and belite-rich cement as a new material that imitates the properties of natural shell material. EVA is used as polymer emulsion. Carbonated polymer-modified cement with a belite-rich cement shows high bending properties. The toughness of the carbonated body is also improved with the addition of EVA. The reaction ratio of cement is related to the absorption amounts of CO_2 in carbonated samples with or without EVA. The reaction of belite is accelerated by carbonation and the addition of EVA compared with the case of water curing.

References

- [1] V.J.Laraia, A.H.Heuer, Microstructures and mechanical behavior of mollusk shells, *Struct. Ceram. Process Microstructure* (1990)79-96
- [2]B.A.Halloran, J.E.Donachy, Characterization of organic matrix macromolecules from the shells of the Antarctic scallop, *Adamussium colbecki*, *Comp.Biochem.Physiol*, 111B(2)(1995)221-231
- [3] T.Maruya, M.Iwanami, E.Sakai, M.Mahsimo, H.Hamada, Durability enhancement of RC structures covered with dense layer formed by marine aquatic fouling organisms(in Japanese), *J. Civil Eng. Soc. Of Japan*,No.739/V-60(2003)61-74
- [4]E.Sakai, M.Morioka, K.Yamamoto, Xi Zhang, Y.Ohba , M.Daimon, Carbonation reaction of hardened low-heat cement (in Japanese),*J.Ceram.Soc.Japan*,107(6)(1999),561-565
- [5]D.A.Silva, P.J.M.Monteiro, Hydration evolution of C3S-EVA composites analyzed by soft X-ray microscopy, *Cem Concr Res*,35(2005)351-357
- [6]E.Sakai, J.Sugita,Composite mechanism of polymer modified cement, *Cem Concr Res* 25(1) (1995)127-135
- [7]S.Kim, H.Taguchi, Y.Ohba, T.Turumi, E.Sakai, M.Daimon, The carbonation of calcium hydroxide and calcium silicate hydrates (in Japanese), *Inorganic Materials* 2(254)(1995)18-25
- [8]D.A.Silva, P.J.M.Monteiro, The Influence of polymers on the hydration of Portland cement phases analyzed by soft X-ray transmission microscopy. *Cem Concr Res* 36 (2006) 1501-1507