

Shrinkage Cracking of Styrene Butadiene Polymeric Emulsion-Modified Concrete Using Rapid-Hardening Cement

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ABSTRACT: This study was performed to resolve the problem of cracks caused by the rapid hydration heat produced during the early setting stages of rapid-hardening cement. To address the hydration heat of rapid-hardening cement, we prepared a modified rapid-hardening cement using calcium sulfoaluminate clinker combined with a styrene butadiene (SB) polymer. The performance of SB polymeric emulsion-modified concrete made from modified

rapid-hardening cement was assessed by determining shrinkage (change in length, and plastic and autogenous shrinkage). The modified rapid-hardening cement in combination with SB polymeric emulsion effectively reduced cracking. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2229–2234, 2009

Key words: latex; rapid-hardening cement; shrinkage

INTRODUCTION

Styrene butadiene (SB) polymeric emulsion in combination with rapid-hardening cement is used for rapid construction. Although rapid-hardening cement can yield high-strength characteristics even in the early stages, fine cracks often occur due to confining pressure from internal/external factors; as the heat of hydration and shrinkage are greater during the early curing stage than in ordinary cement concrete, marked heat and water movement occur inside the concrete. The fine cracks allow water and chloride ions to penetrate the concrete, which leads to various forms of destruction and contributes directly to reduced mechanical properties and durability.^{1,2} In addition, rapid-hardening cement that can be used for immediate construction requires control of the hardening time to allow sufficient work time, so additives such as delaying material, must be input separately. However, when a retarder admixture is input in the field, it can be difficult to control the usage content. Failure to control input content can result in unusable concrete, resulting in work delays. For these reasons,

rapid-hardening cement is often used in small areas but faces limitations in larger areas. Therefore, in this study, we attempted to solve the problems intrinsic to rapid-hardening cement by examining rapid-hardening cement combined with metakaoline in applications for immediate construction and comparing and evaluating how the mixed SB polymeric emulsion affected shrinkage and strength performance.

Problems with existing rapid-hardening cement

The rapid-hardening cement currently used for immediate construction is quick-hardening during clinking, but its long-term strength tends to deteriorate and its strength development rate tends to be reduced due to crystal transitions in the hydration mineral, ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$), resulting in its limited use as a material for immediate reinforcing with assured long-term strength. The clinker of existing rapid-hardening cement can be represented by two kinds of mineral: the first is calcium fluoride containing aluminum ($11\text{CaO}\cdot7\text{Al}_2\text{O}_3\cdot\text{CaF}_2$) or calcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), which is fired and produced at around 1500°C in a rotary kiln. This clinker has stable long-term strength development and excellent strength properties because of the formation of high alumina levels and inclusion of calcium fluoride (CaF_2) on firing. However, work safety is not assured when the molten phase occurs over a certain temperature, and problems can be caused by the volatilization

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TABLE I
Properties of Styrene Butadiene

Solid content (%)	Styrene content (%)	Butadiene content (%)	pH	Specific gravity	Surface tension (dyne/cm)	Particle size (Å)	Viscosity (cps)
46.5	34 ± 1.5	66 ± 1.5	11.0	1.02	30.57	1700	42

of fluorine gas during the firing process. Its long-term development of stable high-strength properties is also limited because of the excessive calcium hydroxide ($\text{Ca}(\text{OH})_2$) in the hardener. The other mineral is calcium aluminate ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3\cdot \text{CaO}\cdot \text{Al}_2\text{O}_3$); because this is produced under amorphous conditions at temperatures above 1600°C in an electric molten furnace, it requires skilled operation of the electric furnace, and thus increases production costs. Its specifications are also difficult to control, and its long-term strength is minimized by the crystal transition of the hydration mineral, ettringite ($3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$).^{3,4} The rapid-hardening cement produced by the latter is designed for use in immediate construction because it acquires practical strength within 3 h. It is based on the fast creation response of ettringite caused by high alumina ingredients or the response of clinker and anhydrite, and thus has a limited usable range as a construction material requiring stable strength development over long periods. The compressive strength of a sample composed mainly of rapid-hardening cement was found to decrease from a peak at 7 days.³ Moreover, this cement exhibits a hydration response because it generates hydration calcium, ettringite, calcium silicic acid hydrate, etc., as it comes in contact with water. Therefore, the level of calcium ions (Ca^{2+}) increases in the liquefied form, reaching a peak after which it decreases. The time taken to reach this peak becomes the starting point of setting, i.e., the generation time of calcium silicic acid hydrate, and thus rapid-hardening cement promotes rapid generation of hydrate, making it difficult to acquire field workability and construction without sufficient control. Therefore, a retarder admixture is used as a compound to delay the supersaturation maximum time, reaching to the peak level of liquefied Ca^{2+} . Generally, use of the retarder admixture chelates Ca^{2+} or creates a hydration shield for cement particles. There-

fore, rapid-hardening cement is often used in the field in conjunction with a separate retarder admixture because otherwise work becomes too difficult, as setting occurs immediately after water is added. In the field, liquid is commonly mixed by dissolving the retarder admixture in water. As the mixture is modified according to the condition of aggregates in the field, it can be difficult to determine the accurate amount of additive. Thus, it is impossible to acquire a certain level of workability and is difficult to obtain consistent product quality.

Composition of rapid-hardening cement

The main component of rapid-hardening cement is calcium sulfoaluminate ($\text{C}_4\text{A}_3\text{S}$; hereafter, CSA) clinker, which has the properties of rapid hardening, high early strength, expansibility, etc., making it useful for various applications, such as rapid-hardening cement and expansion cement. Generally, CSA clinker is produced after firing an admixture of bauxite, lime, and anhydrate at temperatures above 1300°C . The rapid-hardening cement used in this study consisted mainly of CSA clinker (fineness $4000\text{--}5000\text{ cm}^3/\text{g}$) and a fixed amount of metakaoline.

To address the previously discussed problems imposed by existing rapid-hardening cement, we used rapid-hardening CSA clinker, anhydrite, and slaked lime as the main sources to provide rapid hardening and high strength, and Portland cement to provide long-lasting strength. We successfully produced a rapid-hardening cement composite with high strength, which exhibited practical strength within 3 h after commencement of mixing, and simultaneously maintained continuous strength development and long-term stability as well as initial compressive strength. This cement was manufactured for immediate construction, overcoming the decrease in strength

TABLE II
Physical and Chemical Properties of Rapid-Hardening Cement

	Fineness (cm^2/g)	Specific gravity	Setting time (min)		Compressive strength (MPa)			
			Initial	Final	3 h	1 days	28 days	
Physical properties	5161	2.80	30	50	28.3	35.4	54.0	
Chemical properties	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	SO_3 (%)	TiO_2 (%)
	6.2	17.4	0.95	43.9	1.3	0.21	29.3	0.77

TABLE III
Physical Properties of Fine and Coarse Aggregate

Aggregate	Specific gravity			Absorption (%)	F.M.
	Bulk	Bulk (SSD)	Apparent		
Fine aggregate	2.57	2.58	2.61	0.67	2.90
Coarse aggregate	2.80	2.68	2.82	0.35	6.92

caused by the delay in initial mixing hydration due to the addition of SB polymeric emulsion. It has an additional feature of relatively low heat, which does not destroy the SB polymeric emulsion structure during initial high hydration temperatures. In the case of rapid-hardening cement, construction took place with the addition of a retarder admixture, which allowed the necessary delay in hydration response and yielded workability, as it has a fast hydration response during the initial stage. As the quantity of retarder admixture can vary greatly depending on external conditions (temperature, humidity, and wind), it can be very difficult to determine the correct content. To address this problem and acquire a precise work time, we delayed initial setting by adding a powder type of retarder admixture during the process of manufacturing the cement. We successfully produced an easy to handle cement that was not markedly affected by external conditions and yielded sufficient work time. By adding a separate organic acid as a workability control agent, initial strength development was unaffected but the flexibility of the concrete was retained.

EXPERIMENTAL

Materials

SB polymeric emulsion (hereafter, SB latex) was obtained from the Dow Chemical Company (Midland, MI) and used as the compound material. Its features are listed in Table I, while Table II lists the quality test results for the rapid-hardening cement. Crushed aggregate with a maximum size of 13 mm was used as the coarse aggregate, and river sand was used for the fine aggregate; the physical properties of the aggregates are listed in Table III.

Mix proportions

We used a SB latex/cement ratio of 15%, water/cement ratio of 30%, unit cement content of 390 kg/m³, and fine aggregate ratio of 58%, with a target compressive strength of 21 MPa at 3 h and flexural strength of 3.8 MPa at 3 h and 5.0 MPa at 28 days.⁶⁻⁹ The control mix, which was not mixed with SB latex, had a water/cement ratio of 48% and addition of a 1.5% high-range water reducing agent to produce a slump similar to the SB latex mix. We also used rapid-hardening cement combined with a retarder admixture to allow a work time of 25–30 min within the temperature range of 15–20°C. The mixture proportions are shown in Table IV.

Test methods

Setting time and heat of hydration

We measured setting time in compliance with ASTM C-403/C 403M¹⁰ to determine the setting properties of the concrete made with SB latex and rapid-hardening cement. An insulating device was constructed from a styrofoam container and used to test the features of hydration heat development over time after mixing. Mixed concrete at identical temperatures was poured into a 250 mm × 250 mm × 300 mm mold, after which two thermocouples were buried in the center. A data logger measured temperature increases in the concrete at 1-min intervals over 5 h, when the hydration heat reached temperatures close to room temperature.

Length change

We measured length changes in the concrete made with SB latex and rapid-hardening cement in compliance with ASTM C-157/C 157M.¹¹ A test sample measuring 25.4 mm × 25.4 mm × 285.75 mm was produced, demolded in 3 h, and measured immediately; these measurements were used as the standard values. The test sample was cured at a constant temperature (23 ± 2°C) and relative humidity (50 ± 5%); shrinkage was measured and recorded at 5-day intervals over 50 days using a dial gauge.

TABLE IV
Mixture Proportions

Mix	W/C (%)	Latex (%)	S/a (%)	Unit weight (kg/m ³)					
				Water	Cement	Sand	Gravel	SB ^a	SP ^b
Control	48	0	58	187	390	954.70	718.73	–	5.85
SB	30	15	–	51	390	974.37	732.93	124	–

^a Styrene butadiene polymeric emulsion.

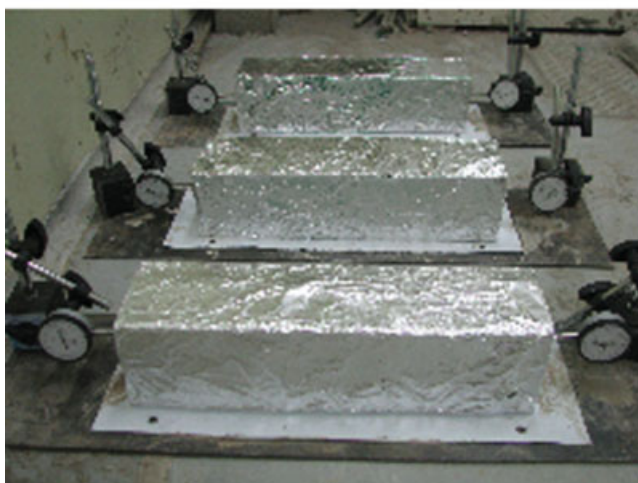
^b Superplasticizer.

Autogenous shrinkage

An autogenous shrinkage test was performed based on the method of Tazawa et al.^{12,13} Free transformation of test samples was ensured by placing a Teflon sheet or polyester film in the 100 mm × 100 mm × 400 mm mold, with a gauge plug at a depth of 30 mm and then constructing each sample from concrete. Samples were demolded after measurement of the amount of shrinkage over 3 h using the dial gauge, taking the shrinkage at the initial setting time of each sample as the standard value. After demolding, the front side of each sample was sealed with thin aluminum adhesive tape, immediately after which shrinkage was measured. The test sample was cured at a constant temperature ($23 \pm 2^\circ\text{C}$) and relative humidity ($50 \pm 5\%$), and shrinkage values were measured at 5-day intervals over 30 days. Figure 1 shows the test before and after demolding.



(a)



(b)

Figure 1 Setup for the autogenous shrinkage test. (a) Before demolding; (b) After demolding.

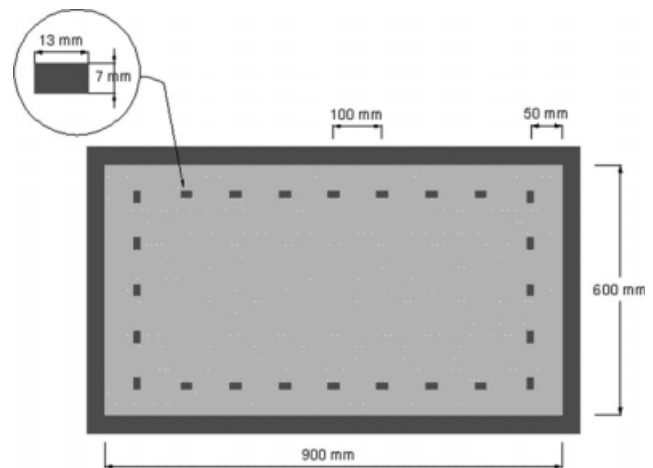


Figure 2 Apparatus for the mortar plastic shrinkage test.

Plastic shrinkage

Cracking caused by plastic shrinkage was evaluated in mortar, which can generate more cracking than concrete. A mix of mortar was applied using the rapid-hardening SB latex-modified concrete mix, with the exception of the coarse aggregate, and testing was performed according to the method of Kraai.^{14,15} Figure 2 shows the mold used in the test, which was a thin plate measuring 900 mm × 600 mm × 150 mm. Tests were performed by applying a restricting condition at intervals of 100 mm, which could create tensile stress around the plate.

Test results and discussion

Setting time and heat of hydration

Figures 3 and 4 show the results of setting time and heat of hydration tests of the concrete mix with SB latex and rapid-hardening cement. The results of the setting time test indicated that adding SB latex delayed setting; the initial setting time of the control mix and the SB mix were 22 and 25 min, respectively, and final setting times were 37 and 40 min, respectively. Addition of SB latex delays setting time

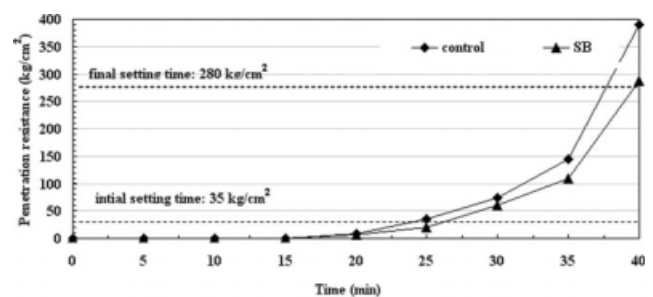


Figure 3 Setting time test.

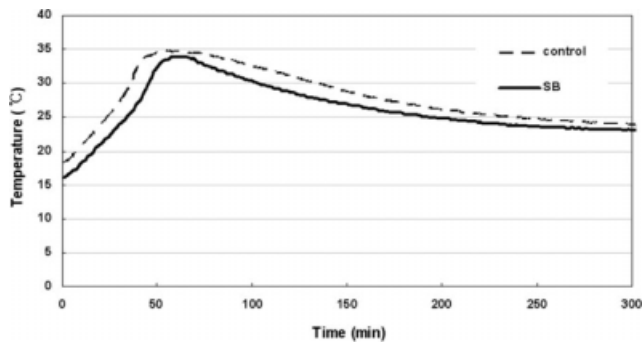


Figure 4 Heat of hydration test.

because it forms a film membrane inside the concrete, delaying the hydration response of concrete and reducing the amount of cement hydration. Ultimately, the rate of cement mixing was reduced, delaying concrete hardening. The results of the hydration heat test revealed that temperatures peaked around 60 min after adding water, and then decreased gradually and approached room temperature at around 300 min. Examination of the maximum temperatures for each mix indicated that the control mix reached a maximum of 34.8°C, whereas the SB mix reached a maximum of 33.8°C. These observations indicated that the hydration heat of the SB mix sample was approximately 3–6°C lower than that of existing rapid-hardening cement. As the main ingredient of rapid-hardening cement is CSA, which can be fired at low temperatures, it should be possible to construct large areas at a relatively low hydration heat by combining rapid-hardening cement with SB latex.

Length change

Tests revealed that the control mix exhibited a change in length of 1221 μm over 50 days. In contrast, the SB mix exhibited a change in length of 771 μm . These observations indicated that the control mix lost a relatively large amount of residual water, as it was designed to have a slump condition identical to the other mix. The control mix continued to shrink over 30 days, and the SB mix exhibited a considerable change over the first day, but its shrinkage was less

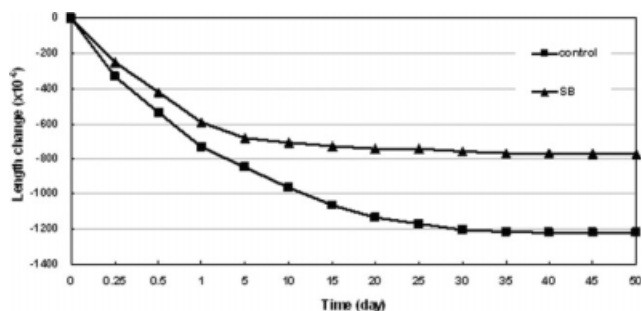


Figure 5 Length change test.

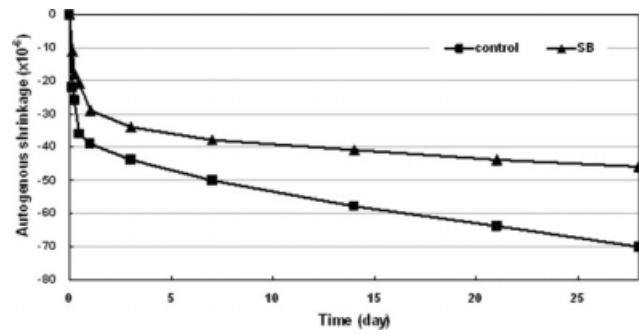


Figure 6 Autogenous shrinkage test.

than that of the control mix and continued gradually increased over 40 days. This phenomenon suggested that the problem of drastic changes in the existing rapid-hardening cement during the initial stage of aging could be resolved by combining the rapid-hardening cement with SB latex. The test results are shown in Figure 5.

Autogenous shrinkage

The results of the autogenous shrinkage test indicated shrinkage of 70 μm in the control mix with no SB latex over 28 days, while that for the SB mix was 46 μm over the same period. As in the mortar length change test, the control mix was designed to have a slump condition identical to the mix combined with SB latex, so this result was due to the loss of a relatively large quantity of residual water. The test results are shown in Figure 6.

Plastic shrinkage

Cracking from plastic shrinkage is greatly affected by the mutually dependent relationship between changes in concrete volume and tensile strength development during the initial setting and occurs when the quantity of bleeding is insufficient to replace evaporated surface moisture. Table V shows the results of the plastic shrinkage test, and Figure 7 illustrates the cracking status of each mix. Only the mix that was not combined with SB latex exhibited considerable cracking from plastic shrinkage, and no cracking appeared in the SB mix. Generally, if SB latex is added to a mixture, it causes cracking from plastic shrinkage. The use of a relatively low water/

TABLE V
Crack Area of Mortar

	Crack length (mm)				Crack area (mm ²)
	3	2	1	0.5	
Control	56.5	99.6	81.0	66.4	482.9
SB	—	—	—	—	—

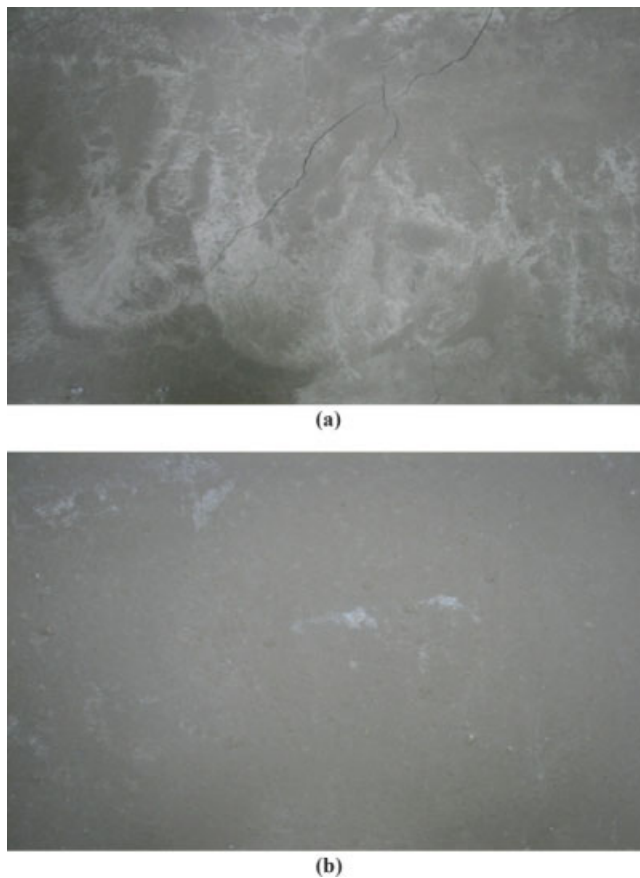


Figure 7 Crack pattern in mortar. (a) Control; (b) SB.

cement ratio and the properties intrinsic to SB latex result in small quantities of bleeding, so evaporated surface moisture is not replaced. However, test results of both mixes indicated that when combined with SB latex, they did not exhibit cracking from plastic shrinkage, and when the retarder admixture and SB latex were combined with the rapid-hardening cement, they helped to reduce surface tensile stress, amount of evaporation, and hydration heat during initial setting.

CONCLUSIONS

We applied laboratory tests to evaluate the properties of shrinkage in SB polymeric emulsion-modified concrete made from rapid-hardening cement. The results can be summarized as follows:

- a. Setting time and hydration heat tests indicated that concrete made from low rapid-hardening cement can produce a relatively low heat of hydration and sufficient work time.

- b. The concrete combined with SB latex did not exhibit cracking after the plastic shrinkage test. As cracking from plastic shrinkage can occur easily due to the small quantity of bleeding to replace evaporated surface moisture and use of a lower water/cement ratio according to the material properties of SB polymeric emulsion, the proposed mixture appears to efficiently minimize cracking.
- c. The mixture with SB polymeric emulsion exhibited relatively small changes in length because of the use of a relatively low water/cement ratio and the SB polymeric film membrane that formed inside the concrete increased the internal confining force.
- d. With regard to autogenous shrinkage, the control mix that did not include SB polymeric emulsion lost a relatively large amount of residue, as revealed by the length change test. Therefore, it showed a greater degree of shrinkage than the SB mix.

These results of shrinkage tests indicated that use of rapid-hardening cement with SB polymeric emulsion can yield minimal shrinkage levels.

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