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Physical and mechanical properties of styrene–butadiene rubber emulsion modified cement mortars

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Abstract

Polymer-modified cement mortars were prepared by varying polymer/cement mass ratio (P/C) with a constant water/cement mass ratio of 0.4. The effect of styrene–butadiene rubber (SBR) emulsion on the physical and mechanical properties of cement mortars is studied. With P/C below 10%, the toughness of the modified mortars enhances with the increase of P/C. A relationship between the physical and mechanical properties of the modified cement mortars at P/C below 10% is found; that is, the compressive strength and flexural strength of the modified mortars are directly proportional to the apparent bulk density. But when P/C is above 10%, the mechanical properties are not highly dependent on the apparent bulk density, and the flexural and compressive strength of the mortars are not improved further with more polymer. Two curing methods [wet cure: 2, 6 or 27 days immersed in 20 °C water; mixed cure: 6 days immersed in 20 °C water followed by 21 days at 20 °C and 70% relative humidity (RH)] were also evaluated in this paper. The results have shown that the mixed cure is more beneficial to the improvement of the mortar properties. A possible mechanism for polymer modification and the relationship between the physical and mechanical properties is proposed based on SEM and IR analyses. The interpenetrating structure between the polymeric phase and cement hydrates forms at a P/C of 8%, and fully develops at a P/C of 10%. The properties of the polymer-modified mortars are influenced by the polymer film, cement hydrates and the combined structure between the organic and inorganic phases.

Keywords: Styrene–butadiene rubber emulsion; Polymer-modified mortar; Physical property; Mechanical property; SEM

1. Introduction

The concept of polymer modification for cement mortar and concrete was put forward before 80 years [1,2]. Since then, considerable research and development of polymer modification for cement mortar and concrete have been conducted in various countries. As a result, many effective polymer modification systems for cement mortar have been developed and are already used in various applications in the construction industry.

Polymer-modified mortar is a good repair material for its many excellent properties, such as the same production progress with cement mortar, good mechanical properties, especially bond strength and toughness, and good durability [3,4]. In this field, polymer latexes have been widely used and prove to be very good [5]. Although the properties of cement mortars can be improved by adding polymer latex, the polymer modification mechanism is not clear and still much research should be done.

Styrene–butadiene rubber (SBR) emulsion is widely used to modify cement mortar. The former researches showed that SBR-modified mortars had good mechanical properties [6,7], antipenetrability [8,9] and frost resistance [10]. A late report said SBR could be used to make self-leveling materials [11]. But it seems that few reports on the relationship between its physical and mechanical properties are found until now. Our previous work

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indicated that SBR emulsion could reduce water/cement ratio, effectively enhance both flexural strength and tensile bond strength, substantially decrease the ratio of compressive strength to flexural strength and improve the ratio of flexural strength to elastic modulus. The prepared SBR-modified mortar is suitable for bridge repair [12,13]. At the same time, it was found that the porosity of the hardened mortar had relation with the bulk density of the fresh mortar to a certain extent; the compressive strength, flexural strength and elastic modulus had some relations with the porosity and bulk density [14]. But further work should be done to prove whether the rule is ubiquitous. Thus, the effect of SBR emulsion on the physical and mechanical properties of cement mortars with same water/cement mass ratio and the relationships between them are studied in this paper, and the polymer modification mechanism is explored.

2. Experimental

2.1. Materials

Portland cement type P II 52.5R, according to Chinese standard GB 175, and standard sand, according to ISO 679, were used for preparing the specimens. The chemical composition and physical properties of the cement are listed in Tables 1 and 2, respectively. The Styrofan SD622S styrene–butadiene rubber (SBR) emulsion (viscosity: 30 mPa·s; Tg: 11 °C; pH: 9.5; solid content: 47%) and deionized water were used in the experiment.

2.2. Specimen preparation and test methods

2.2.1. Polymer-modified mortars

The mortar specimens were prepared with polymer/cement mass ratio (P/C) of 1–20%, water/cement mass ratio of 0.40 and sand/cement mass ratio of 3. The polymer emulsion was added to water firstly, then specimens with the dimension of 40×40×160 mm were prepared according to GB 17671 (ISO 679). The specimens were demolded after 1 day. Two curing methods [wet cure: 2, 6 or 27 days immersed in 20 °C water; mixed cure: 6 days immersed in 20 °C water followed by 21 days at 20 °C and 70% relative humidity (RH)] were used.

2.2.2. Apparent bulk density

The apparent bulk density is the bulk density of the cured specimens prepared in Section 2.2.1 with surface dried by moist soft towel.

2.2.3. Mechanical properties

The compressive and flexural strengths were determined according to GB 17671.

2.2.4. SEM observations

SEM observations for the characterization of the polymer-modified mortars were carried out at the age of 28 days using a HITACHI S2360N SEM. The samples, taken at a depth of >5 mm from the surfaces of the cured specimens, were cleaned with ethanol and then dried in vacuum until the weight becomes changeless. After drying, the cross-sections of the samples were etched with 1% hydrochloric acid (HCl) for 2 min. Then, the samples were dried again and coated with gold.

2.2.5. FTIR analysis

FTIR spectra were recorded on a Bruker EQUINOX 55 spectrophotometer over the wavelength range of 400–4000 cm^{-1} using the potassium bromide disc technique. The dried samples, the same as that said in SEM observations, were grinded and then sieved with a 45-μm sieve.

3. Results and discussion

3.1. Apparent bulk density of polymer-modified mortars

The apparent bulk density of mortars is closely related to its properties. Thus, the effect of polymer on the apparent bulk density of polymer-modified mortars is studied firstly. The relationship between the apparent bulk density of the modified mortars and P/C is shown in Fig. 1. It is found that the apparent bulk density of the 7-and 28-day wet-cured modified mortars rises slightly at the P/C of 1–2%, then declines with increasing P/C, whereas the apparent bulk density exhibits few dependency on P/C between 7% and 10%, followed by an increment until to P/C of 20%. The change of the apparent bulk density of 3 days wet-cured modified mortars with P/C is similar to that of 7 or 28 days wet-cured, except for no rise at the P/C of 1–2%. The influence of curing methods on the relationship is slight, but the apparent bulk density of the mixed-cured modified mortars is lower than that of wet-cured at the same P/C. It may be ascribed to the more water lost at the mixed-cured conditions.

3.2. Mechanical properties of polymer-modified mortars

3.2.1. Compressive strength

The compressive strength of polymer-modified mortars with different P/C is illustrated in Fig. 2. It is seen that the

Table 1
Chemical composition of P II 52.5R Portland cement

Component	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	TiO_2	BaO
Content (%)	21.3	65.1	5.1	2.9	1.1	1.8	0.7	0.2	0.3

Table 2
Physical properties of P II 52.5R Portland cement

Specific gravity (20 °C), (g · cm^{-3})	Fineness		Setting time		Flexural strength of mortar (MPa)			Compressive strength of mortar (MPa)		
	Residue on sieve of 80 μm (%)	Blaine's specific area (m^2 · kg^{-1})	Initial set (h)	Final set (h)	3 days	7 days	28 days	3 days	7 days	28 days
3.20	0.5	385.50	2.05	3.17	6.94	7.77	8.43	39.04	48.98	60.62

compressive strength of the wet-cured modified mortars declines with the increase of P/C between 1% and 8%, and then hardly changes. The longer the cured ages, the higher the compressive strength of the wet-cured modified mortars. This may be attributed to that the long cured time is helpful for the cement hydration and the formation of the polymer film in mortars. The compressive strength of the mixed-cured modified mortars sharply increases at the P/C of 1–2%, and then the variation of the compressive strength with P/C is similar to that of wet-cured mortars. However, the compressive strength of the mixed-cured mortars is higher at a same P/C.

3.2.2. *Flexural strength of polymer-modified mortars*

The flexural strength of the wet-cured modified mortars with different cured ages rises slightly at the P/C of 1–2%, then declines with growing P/C until it reaches 7% as shown in Fig. 3. The flexural strength is hardly dependent upon the P/C range of 8–10%. However, the change of the flexural strength with increasing P/C is different for the mortars with different cured ages at P/C above 10%: it decreases for 3 days, hardly changes for 7 days and goes up for 28 days. The longer cured age makes the flexural strength higher at the same P/C. For the mixed-cured modified mortars, the flexural strength rises remarkably when a small amount of polymer is added, and then slightly declines. When the P/C is higher than 8%, the flexural strength goes up again. All the flexural strengths of the mixed-cured modified mortars are higher than that of the control mortar, indicating that the mixed cure is more helpful for the development of the flexural strength. This must be due to the easier polymer film formation and to the higher degree of cement hydration under this curing condition.

3.2.3. *Toughness of polymer-modified mortars*

The ratio of compressive strength to flexural strength of mortars is an important factor to judge its toughness. Fig. 4 shows the ratio of the compressive strength to flexural strength of the modified mortars with different P/C. It is found that the ratio drops sharply with increasing P/C up to 8%. At higher P/C ratios, the results are not obvious. When P/C is above 10%, the ratio rises slightly for 3- or 7-day wet-cured modified mortars, but declines slightly for 28-day wet-cured mortars. When mixed cure is used, the ratio of the compressive strength to flexural strength sharply decreases with higher P/C (up to 10%), and then hardly changes with further increment of P/C. The above results suggest that the toughness of the modified mortars can be improved markedly at P/C below 10%. The higher the P/C ratio, the better the toughness for P/C ratios smaller than 10%. When P/C ratio is higher than 10%, the effect on the toughness is slight. The results indicate that the mixed cure is better for the improvement of the toughness.

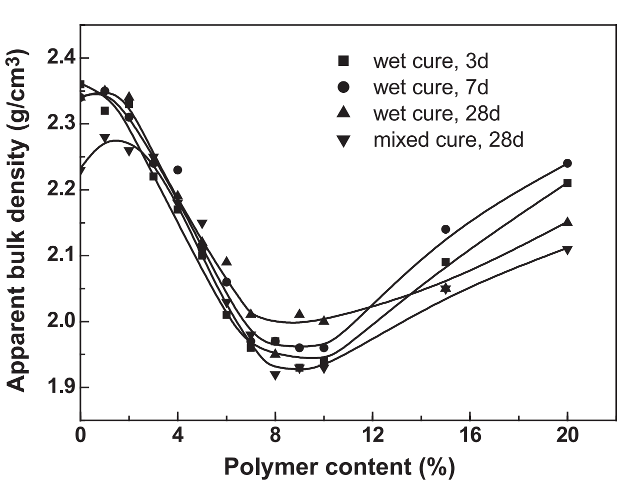

Fig. 1. Relationship between the apparent bulk density of polymer-modified mortars and polymer/cement mass ratios (P/C).

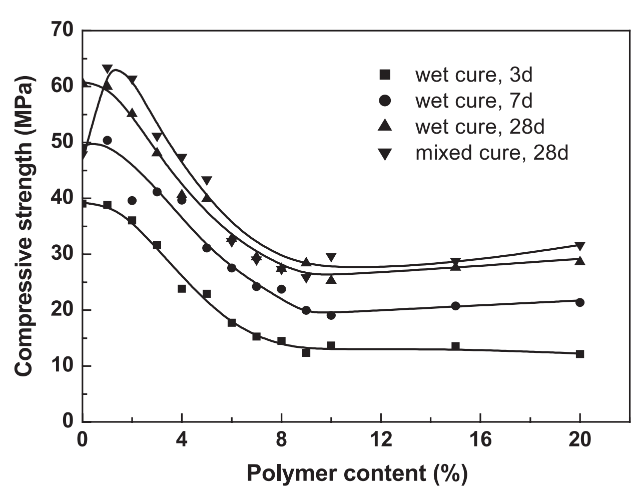

Fig. 2. Compressive strength of polymer-modified mortars with different polymer/cement mass ratios (P/C).

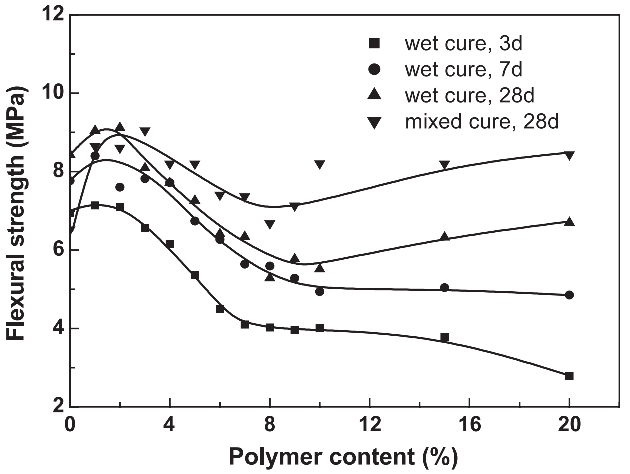

Fig. 3. Flexural strength of polymer-modified mortars with different polymer/cement mass ratios (P/C).

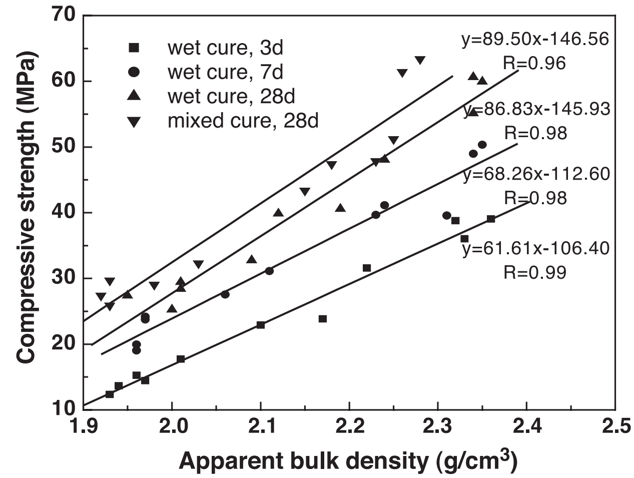

Fig. 5. Relationship between the compressive strength and apparent bulk density of polymer-modified mortars (P/C<10%).

3.3. Relationship between the physical and mechanical properties of polymer-modified mortars

The relationships between the compressive and flexural strength and the apparent bulk density of polymer-modified mortars at P/C below 10% are illustrated in Figs. 5 and 6, respectively. It is clear from these figures that the compressive and flexural strengths of the modified mortars are directly proportional to the apparent bulk density no matter what curing age and method are used; that is, the strength rises linearly with the apparent bulk density. From the slope of the line, it is seen that the rise of the compressive and flexural strengths with increasing apparent bulk density is faster for 28-day than for 3- or 7-day wet-cured mortars. The compressive and flexural strengths of the modified mortars increase with prolongating cured ages at the same apparent bulk density. The growing rate of the compressive strength with the apparent bulk density of the mixed-cured modified mortars is close to that of 28 days wet-cured, but that of its flexural strength is slower. Nevertheless, both the compressive and flexural strengths of the mixed-cured modified mortars are higher at the same apparent bulk density. It implies that the cement hydration and polymer film are also important factors for the compressive and flexural strengths of the modified mortars, except for the apparent bulk density.

In our experiment, it is found that the strength of the modified mortars is not highly dependent on the apparent bulk density at P/C above 10% and the relationship between them is no longer coincident with the linearity at P/C below 10%.

3.4. Mechanism of polymer modification

Fig. 7 shows the SEM microphotos of the fracture surfaces of the 28-day wet-cured polymer-modified mortars.

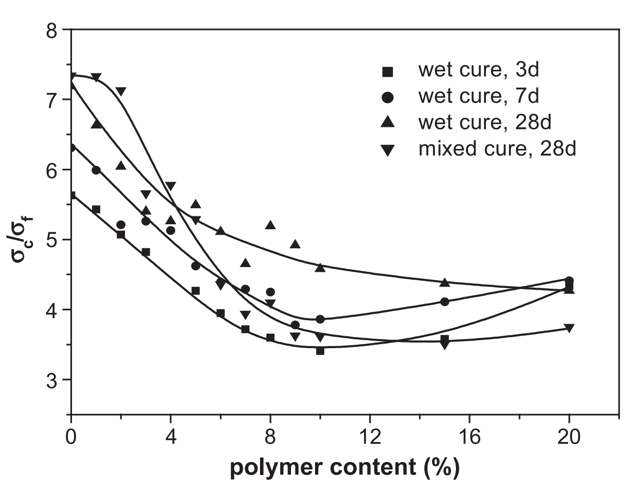

Fig. 4. Ratio of the compressive strength to flexural strength (σ_c/σ_f) of polymer-modified mortars with different polymer/cement mass ratios (P/C).

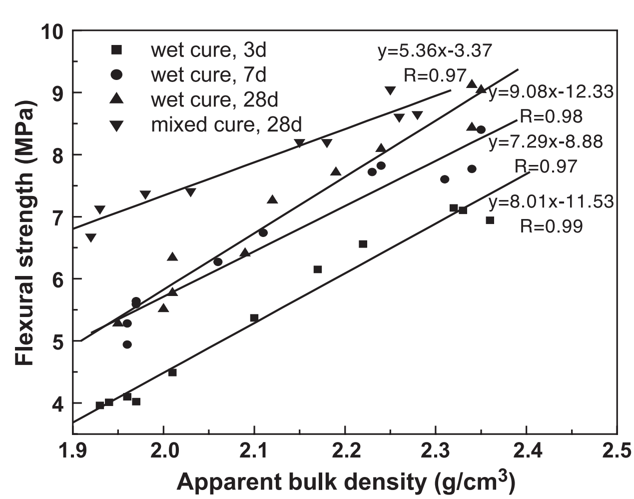

Fig. 6. Relationship between the flexural strength and apparent bulk density of polymer-modified mortars (P/C<10%).

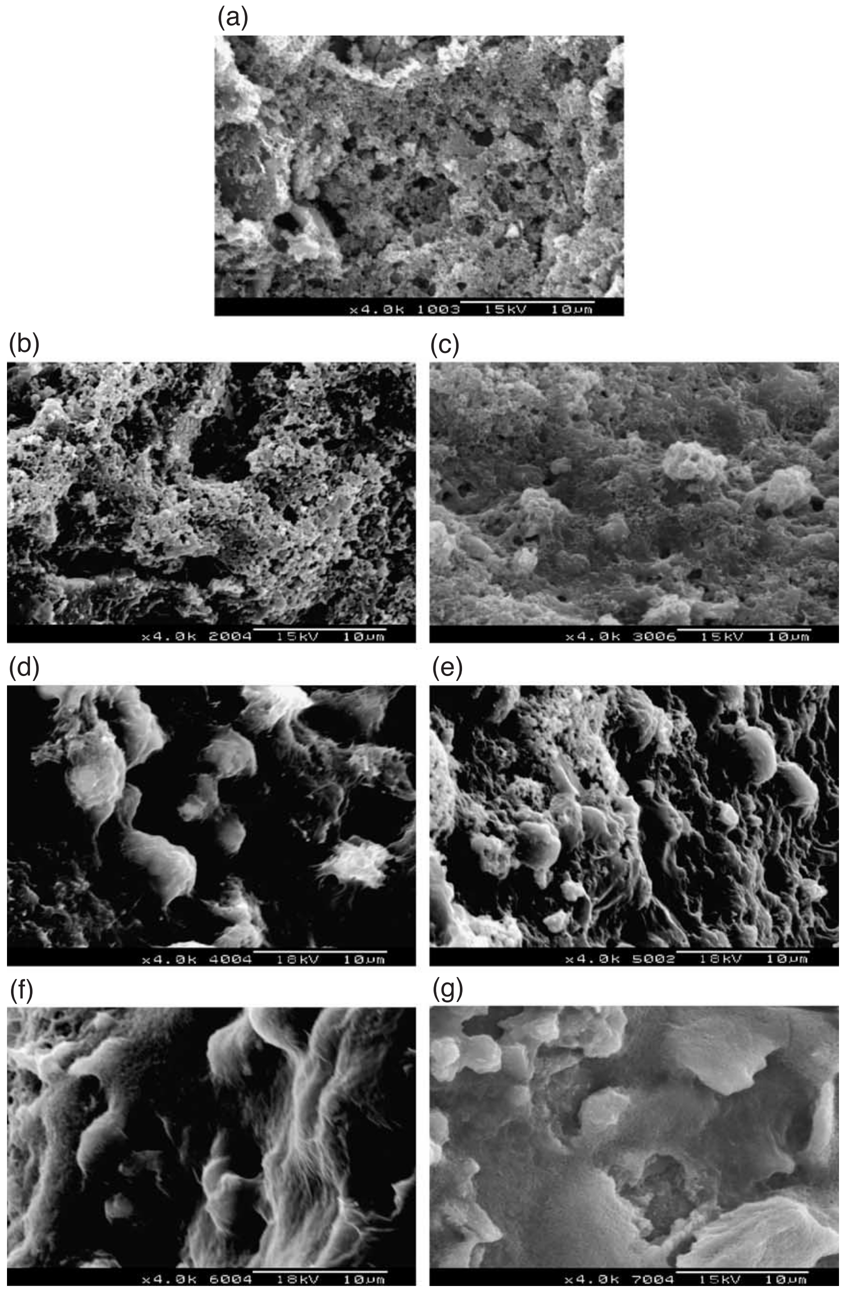

Fig. 7. Fracture surface of 28-day wet-cured polymer-modified mortars at polymer/cement mass ratio (P/C) of (a) 0%, (b) 1%, (c) 5%, (d) 8%, (e) 10%, (f) 15% and (g) 20% (2 min etching with 1% HCl solution).

(a) is the SEM of the control mortar, (b) to (g) are the SEM of the modified mortars at the P/C of 1%, 5%, 8%, 10%, 15% and 20%. The SEM analysis exhibits that the constituents of the control mortar are loosely joined with each other (a). By contrast, the structure of the mortar is compactly joined with each other when 1% polymer is added, although no polymer film is formed (b). Some scattered polymer films are found in the fracture surface of the modified mortar at a P/C of 5% (c). Coherent polymer film forms in the modified mortar at a P/C of 8%, and the lost inorganic phase is also coherent, so the interpenetrating structure between the polymer and cement hydrates forms (d). And the structure fully develops when P/C reaches 10% (e). When P/C is above 10%, the formed polymer film in the modified mortars becomes thicker and the structure of the modified mortars is still interpenetrating (f and g).

From the FTIR spectra of the 28-day wet-cured polymer-modified mortars (Fig. 8), it is seen that the FTIR spectra hardly change with P/C below 10%. However, at P/C higher than 10%, the absorption peak at 3644cm^{-1} decreases, which corresponds to the -OH of $Ca(OH)_2$, and the peaks at 1079 and 996 cm^{-1} also change, the former increases and the later decreases, which corresponds to the SiO_4 tetrahe-

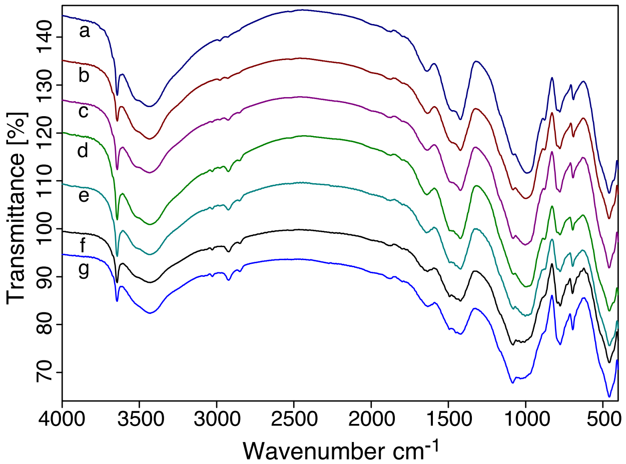

Fig. 8. FTIR spectra of 28-day wet-cured polymer-modified mortars at polymer/cement mass ratio (P/C) of (a) 0%, (b) 1%, (c) 5%, (d) 8%, (e) 10%, (f) 15% and (g) 20%.

dron. That indicates the structure of the SiO_4 tetrahedron changes and the cement hydration is influenced.

Polymer has better water retention property and can increase the porosity of mortars [15]. Most former studies are about composites with P/C≥5%. However, we think the polymer can fill the holes of the mortar, reducing its porosity at P/C of 1–2%, because polymer particles in mortars are difficult to coalesce at the lower P/C (Fig. 7(b)). It is the reason for the increase of the apparent bulk density at the P/C of 1–2%. Of course, the flow of the control mortar is smaller than that of the modified mortar, which also inclines to make the density of the control mortar low (Table 3).

It can be concluded that the properties of the polymer-modified mortars are influenced by its phase state, i.e., the polymer film, cement hydrates, and the combined structure between the organic and inorganic phases. The cement hydration and polymer film in the modified mortars develop with prolongating cured age, which results in enhanced strength. The structure of the mortar essentially changes when coherent polymer film forms. In this case, the interpenetrating structure forms in the modified mortars. The coherent polymer film reduces weakness in the mortars, prevents extending of the tiny cracks, and drops the rigidity of the mortars. As a result, the polymer takes good effect in improving the toughness of the mortars. If more polymer is added after the fully developed interpenetrating structure forms, the polymer film will become thicker and the structure of the mortars is still interpenetrating. Moreover, the higher P/C affects the cement hydration. Thus, the properties of the mortars are not improved further with the increment of P/C above 10%. It also reveals why the relationship between the strength and the apparent bulk density at P/C above 10% is no longer in accordance with the linearity at P/C below 10%.

SBR film is very tough, like rubber for SBR comprising both the flexible butadiene chains and the rigid styrene chains. The hardened cement mortar is rigid. Their properties complement each other. As a result, polymer-modified mortar composites with excellent properties can be achieved when the P/C is appropriate.

4. Conclusion

With the same water/cement mass ratio, the apparent bulk density and compressive and flexural strengths of the polymer-modified mortars rise slightly when a little SBR emulsion is added, and then all of them decline with increasing P/C. But when P/C is above 10%, the apparent bulk density grows with increasing P/C and the strength hardly changes. The toughness of the modified mortars can be improved markedly and the higher the P/C, the higher the toughness at P/C below 10%. The compressive and flexural strengths of the modified mortars have good relations with the apparent bulk density at P/C below 10%; that is, they are directly proportional to the apparent bulk density. With P/C above 10%, the polymer films in the mortars become thicker, and the flexural and compressive strengths are not improved further. The relationship between the strength and apparent bulk density of the modified mortars at P/C above 10% is no longer coincident with the linearity at P/C below 10%. The interpenetrating structure between the polymer and cement hydrates forms at a P/C of 8%, and fully develops at a P/C of 10%. The properties of the polymer-modified mortars are influenced by the polymer film, cement hydrates, and the associative structure between the organic and inorganic phases. The mixed cure is more beneficial to the improvement of the mortar properties.

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Table 3
Flow table values of polymer-modified cement mortars (tested according to Chinese standard GB/T 2419-1994)

P/C	0	1	2	3	4	5	6	7	8	9	10	15	20
Flow table value (mm)	110	127	141	152	164	178	190	205	223	236	250	>260	>260

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