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Utilization of steel slag, iron tailings and fly ash as aggregates to prepare a polymer-modified waterproof mortar with a core–shell styrene–acrylic copolymer as the modifier

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HIGHLIGHTS

- A new polymer-modified waterproof mortar was prepared using steel slag, iron tailings and fly ash as aggregates.
- A core–shell styrene–acrylic copolymer was used as the mortar modifier.
- The mortar gave better mechanical properties and water resistance compared to those with commercial EVA and SAE as modifier.

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ABSTRACT

Using Poly(styrene-co-hydroxyethyl methacrylate) (P(St-co-HEMA)) microsphere with a core–shell structure as the modifier, a new polymer-modified waterproof mortar was developed with steel slag, iron tailings and fly ash as aggregates. Effects of cement–aggregate ratio, polymer–cement ratio and defoamer–cement ratio on performances of this mortar were investigated. The factor design was used to determine the optimal conditions: polymer–cement ratio, 12 wt.%; cement–aggregate ratio, 1:2.5; defoamer–cement ratio, 0.8 wt.%. The product conformed to Chinese norms. Furthermore, the mortar with P(St-co-HEMA) as the modifier gave better mechanical properties and water resistance compared to those with commercial ethylene–vinyl acetate copolymer (EVA) and styrene–acrylic copolymer (SAE) as modifiers. Microstructures of these polymer-modified mortars were compared and discussed.

1. Introduction

The polymer-modified waterproof mortar is developed by adding the polymer composition to common cement mortar. With the synergistic effect between inorganic and organic materials, some defects of traditional rigid waterproof materials including low flexural strength, low bond strength, easy cracking and poor water resistance can be improved. Therefore, the polymer-modified waterproof mortar has drawn more and more attention these years [1–8]. The general modifiers include ethylene–vinyl acetate copolymer (EVA), polyacrylic ester (PAE), traditional styrene–acrylic copolymer (SAE), etc. Among them, SAE can increase the flexural strength and bond strength of mortar [9,10]. It also has the advantages of little pollution and low cost [11]. However, SAE is generally prepared by emulsion polymerization with small molecular surfactant as the emulsifier, which can affect the mechanical strength and impermeability of mortar. So its application is restricted [9–12]. Much attention has been paid to modification of SAE in terms of polymerization process and polymer structure.

Aggregates in the mortar have a significant impact on material workability, strength, shrinkage and cost. The river sand is generally used as aggregate to prepare the waterproof mortar. However, with the rapid development of construction industry, a large amount of river sand is consumed. The storage of river sand falls sharply in China, and great exploitation of river sand seriously affects the ecological safety of river. In addition, a large amount of steel slag and iron tailings are produced with the rapid development of iron and steel industry in China, which have led to a serious environmental deterioration. Therefore, using these solid waste materials to replace river sand as mortar aggregate is beneficial to saving resources and protecting the environment. Replacement of river sand with iron tailings in the preparation of

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building materials has been reported recently [13–18]. The replacement level is generally controlled at 50 wt.% or less [14,15]. However, use of steel slag as a construction material has been a problem as free CaO and/or MgO abundant in steel slag expand during hydration [19]. Particular care must be taken to prevent potential steel slag expansive behavior in confined applications. Its expansion risk is minimal when free CaO and MgO content is limited (less than 5%) and when steel slag is exposed in outdoor conditions for a period longer than 9 months [20,21]. Some studies have been conducted on the utilization of coarse slag as coarse aggregate in the concrete [22–32]. Besides, Qasrawi et al. [33] used fine slag as fine aggregate replacing the sand in the mixes, partly or totally. However, to the best of our knowledge, the utilization of steel slag as aggregate in the preparation of polymer-modified waterproof mortar has not been reported.

In this paper, the core–shell poly (styrene-co-hydroxyethyl methacrylate) copolymer (P(St-co-HEMA)) was synthesized by emulsifier-free emulsion polymerization. This core–shell structure could make the functional monomer hydroxyethyl methacrylate (HEMA) mainly exist on the surface of the polymer particle. The amount of HEMA was reduced largely. It was beneficial to polymer's low cost and high functionality. Using steel slag, iron tailings and fly ash as aggregates, a new polymer-modified waterproof mortar was developed with this P(St-co-HEMA) microsphere as modifier. The products will have both environmental and economic benefits.

2. Materials and methods

2.1. Materials

The monomer styrene (St) and HEMA were readily available on the market. EVA, SAE, iron tailings, steel slag, fly ash and ordinary Portland cement were provided by local suppliers. The fineness modulus of the iron tailings was 0.81. Steel slag was sieved and the used size was less than 0.3 mm. Chemical compositions of steel slag and iron tailings are listed in Table 1. The strength class of ordinary Portland cement was 42.5 in accordance with Chinese Standard GB 175-2007 [34] (the equivalent standard is ASTM C150 [35]). Water reducing agent was naphthalene sulfonate, and tributyl phosphate was used as the defoamer.

2.2. Preparation of P(St-co-HEMA) microsphere

P(St-co-HEMA) microsphere was prepared by a soap-free emulsion polymerization in a 1000 ml four-neck reactor equipped with a reflux condenser, a mechanical stirrer and a thermometer under nitrogen atmosphere. St and a mixed aqueous solution of NaOH and $NaHCO_3$ were added to the reactor with a fixed proportion. When the temperature rose to 75 °C, potassium persulfate was added to initiate the polymerization and allowed to polymerize for 5 h. Then, HEMA was introduced. After 3 h copolymerization, the core–shell P(St-co-HEMA) microspheres were obtained by centrifuging and drying.

2.3. Characterization of polymers

Gas chromatography (GC950) was used to determine the contents of residual monomers (St and HEMA) by using tetradecane as internal standard. Then the monomer conversions were obtained and compositions of P(St-co-HEMA) were estimated. The compositions of EVA and SAE were determined using ^1H NMR with $CDCl_3$ as the solvent. The average hydrodynamic diameter of polymer particle was measured by the Laser Particle Size Analyzer (Zetasizer Malvern 3000HSA). The morphology of polymers was characterized using the Transmission Electron Microscope (TEM, Jeol 100CX-II) and Scanning Electron Microscope (SEM, S-4800-I).

2.4. Preparation and testing of the polymer-modified waterproof mortar

The polymer-modified waterproof mortar was developed by mixing P(St-co-HEMA) microsphere, iron tailings, steel slag, fly ash and additives. The water reducing agent was 0.5 wt.% (by the mass of cement). This mixture was then mixed with water to make the test specimens. Water requirement was obtained by controlling the consistency (70 ± 5) mm. The setting time, consistency, mechanical strength, impermeability, bond strength, flexibility, alkaline resistance, heat resistance, freeze–thaw and shrinkage tests were carried out according to Chinese Standard JC/T984-2011 [36] (the equivalent standards are ASTM C1438 [37] and C1439 [38]). The morphology of mortar was characterized by SEM. The radioactivity test was done according to Chinese Standard GB/6566-2010 [39].

3. Results and discussion

3.1. Characterization of EVA, SAE and synthesized P(St-co-HEMA) microsphere

Through the above preparation process, the P(St-co-HEMA) microsphere with a core–shell structure was obtained. Its minimum film-forming temperature is 5 °C. The TEM image is shown in Fig. 1. Its core was PS and shell was St-HEMA copolymer. This core–shell structure could make functional monomer HEMA mainly exist on the surface of microspheres. The added amount of HEMA was reduced largely. It was beneficial to polymer's low cost and high functionality. SEM images for EVA, SAE and P(St-co-HEMA) are showed in Fig. 2. It can be observed that, EVA particles were heterogeneous and very large particles were present. Compared with EVA, the synthesized P(St-co-HEMA) microspheres had smaller particle size and better homogeneity. SAE had similar particle size with P(St-co-HEMA). However, P(St-co-HEMA) was more homogeneous than SAE. Besides, the adhesion of SAE particles was serious, and some impurities such as emulsifiers were present on the particle surface. The particle size determined by DLS (Dynamic Light Scattering) and compositions estimated by gas chromatograph (for synthesized polymers) or ^1H NMR (for EVA and SAE) are listed in Table 2.

3.2. Preparation and properties of P(St-co-HEMA) modified waterproof mortar

3.2.1. The aggregate composition

Iron tailings, steel slag and fly ash were used to replace river sand for preparing the mortar. For determining a reasonable ratio of them, effects of the aggregate ratio on mechanical properties of mortars were investigated. As shown in Table 3, iron tailings was fixed to 40 wt.% and the content of steel slag was ranged from 30 to 60 wt.%. The strength results for these mortars are listed in Table 3.

As seen in Table 3, both flexural strength and compressive strength were increased with an increase in the steel slag content from 30 to 50 wt.%. This indicated that the addition of steel slag in this content range was beneficial to the mechanical performances of mortar. However, when river sand was completely replaced by steel slag, both flexural strength and compressive strength decreased sharply. The possible reason is that, stability problems may appear as the steel slag content is high enough, after steam-cured 7 h in the pressure autoclave. Therefore, 20 wt.% fly ash was used to replace part of steel slag as shown in Entry 5. This

Table 1
Chemical composition of iron tailings and steel slag.

	Chemical composition (wt.%)								
	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	MnO	f-CaO	Loss on ignition
Iron tailings	13.03	9.09	55.62	11.03	11.42	1.77	–	–	2.17
Steel slag	40.35	7.50	17.30	20.13	6.29	0.36	3.73	2.58	1.67