Development of Polymer Modified Cement Mortars for Waterproof

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Abstract. The paper describes the raw materials and properties of polymer modified cement mortars for waterproof. In this paper, the following aspects were discussed, the effect of different polymer cement ratio on the ratio of compressive strength to flexural strength, the mechanism of the improvement of impermeability, durability and viscosity by the cooperation of super mineral powder and re-dispersible powders respectively. In addition the effect of graded sand and fiber on the cracking resistance and contractility of mortar were also studied.

1. Introduction
With ever demanding requirements for quality of building engineering and use function of buildings, wall and moisture base surface waterproofing becomes a concern and focus by architectural sector. In the traditional waterproofing concept, rigid waterproofing is generally deemed as an auxiliary function of building structure, so the focus is structure self-waterproofing or dense and thick concrete waterproof layer (generally 40mm thick) closely connected to structure; flexible waterproof materials such as membrane, sheet and coating are applied in engineering as independent waterproof materials. These flexible materials have their respective advantages, for instance, good deformability and easy to be applied on large-scale plans. However, such materials are demanding on base course dryness, and water content is limited within 9%, which is hard to be realized in underground engineering, especially deep-seated basement; coating applied in elevation is convenient, but membrane and sheet construction is much more difficult, and the problem lies in secondary decoration after membrane and sheet are applied on elevation. It is hard to directly adhere facing tiles or veneer onto flexible waterproof layer, which is proved by experiences and lessons. It is safe to say that flexible waterproof materials are unsuitable in elevation and wet base surface waterproof engineering.

In recent years, during large-scale development of urban underground space and renovation, restoration and utilization of a number of underground civil defense engineering, downstream face construction method is adopted, utilizing both rigid and flexible materials and multi-layer waterproofing method, so market demand for waterproof mortar is large as such mortar can be adopted in downstream face and upstream face waterproof construction, in underground, roof and external wall waterproofing works, and on humid base surface. However, several problems have been found during the application of rigid waterproof mortar in engineering, like weak impermeability, high water absorption and dry shrinkage rate, and easy to crack.

At present, waterproofing agent and other measures have been adopted to block water seepage gallery, which helps removing concrete and cement mortar defects to some extent, but the effect is not desirable as internal structure of material is not changed. In particular, it cannot meet waterproof requirement for building if served as the waterproof layer.
2. Study on performance of polymer polymer waterproof mortar

Polymer polymer waterproof mortar is a kind of waterproof material which is mainly composed of cement and fine aggregates, mixed with polymer, admixture and other modified materials based on an appropriate proportion. Such mortar is divided into dry powder (Type I) and emulsion (Type II), based on different states of polymer modified materials. This test object is dry powder (Type I) mortar consisting of Portland cement, fine aggregate, polymer dry powder, expanding agent super-plasticizer, ultrafine powder and other admixtures. Such mortar has high cohesive strength and impervious impermeability, and is an excellent rigid impervious waterproof material and easy to operate. Before using, add water and stir evenly.

2.1. Cementing material

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2.1.1. Inorganic cementing material-cement. Cement is an inorganic cementing material for polymer cement mortars for waterproof. On the one hand, cement as a kind of hydraulic cementing material can improve cohesive strength of coating. On the other hand, a mixture of cement and polymer powder can further improve water resistant performance of polymer cement under synergy effect of active cation and hydrophilic anion in powder. Considering a balance between waterproof mortar strength and constructability, as well as the influence of different types of cement on comprehensive performance of waterproof mortar and upon test, P.O42.5 ordinary Portland cement is selected as the inorganic cementing material for polymer cement waterproof mortar based on test.

2.1.2. Selection of re-dispersible glue-powder. The types, structural forms and distribution of re-dispersible glue-powder can significantly affect structure and performance of hardened waterproof polymer cement mortar. Polymer-cement mortar is generally divided into three parts: set cement, polymer and pore. Hardened mortar is mainly composed of set cement and polymer, which are bonded on interface between inorganic particle and polymer particle in mortar structure. Performance of polymer in the mortar depends on binding form of polymer glue powder and cement as well as their mutual cementation. At present, main types of glue powders adopted include ethylene-acetate ethylen copolymerized emulsion powder. Table 1 compares their performances in waterproof polymer cement mortar.

| Type       | 801  | 2488 | PV-23 | 5603P | 115L  |
|------------|------|------|-------|-------|-------|
| Cohesive strength (Mpa) | 7d   | 0.6  | 0.8   | 1.0   | 1.3   |
| Cost       | Low  | Relatively low | Moderate | Moderate | Relatively high |

Based on the above the table, PV-23, 115L and 5603P shows good original strength and water-resisting strength, of which, the first two are inferior while prices of the latter two are higher, so 5603P has the best performance-to-price ratio. 5603P is a kind of re-dispersible vinyl acetate-ethylene copolymerized emulsion powder, which is of low vitrification temperature and higher flexibility, so it is applicable to waterproof polymer cement mortar.

2.1.3. Influence of different polymer-cement ratios on performance of waterproof polymer cement mortar. Influence of different polymer-cement ratios on performance of waterproof polymer cement mortar under the same test conditions. Figure 1 shows that larger polymer-cement ratio will lead to a significant increase of cohesive strength and ratio of compressive strength to flexural strength; when polymer-cement ratio is 0.06-0.1, cohesive strength of mortar is 1.7Mpa and ratio of compressive strength to flexural strength is 2.8. The reason is that hydrophilic polymer and liquid phase of cement
base holes and pores, polymerize to form film, and firmly absorb on the base surface, thus guaranteeing good and firm bonding between mortar and base. Polymer modified cement involves two processes: cement hydration and film formation of polymer. Cement hydrates firstly, and then condensate and harden, while dehydrated polymer will form a film attached to hydrated cement particles and realize a linear polymerization between pores which constitutes mutual continuous phase with set cement. It can obviously improve cohesive strength and flexibility of mortar and reduce ratio of compressive strength to flexural strength.

Figure 1. Influence of different polymer-cement ratios on performance of waterproof polymer cement mortar

2.1.4. Influence of synergy effect of super mineral powder and re-dispersible glue-powder on mortar impermeability. Ordinary mortar has high porosity but poor anti-permeability. Test proves that the synergy effect of super mineral powder-microsilica and emulsion powder can significantly improve anti-permeability of mortar. The synergy effect mechanism is physical and chemical reactions on surface, which is a very complex process, and is manifested in two aspects: firstly, surface active agent is absorbed onto super mineral powder surface, electric potential is enhanced and such actions as water reduction, dispersion, plastication, filling and homogenization on cement mortar can be improved. The combination of surface active agent and super mineral powder contributes to form a compact microstructure of cement mortar. In addition, the introduction of glue powder and super mineral powder-microsilica can greatly reduce weepage and improve pore structure; secondly, microsilica can replace glue powder to fill internal void and defect in cement mortar structure, so that glue powder is used to fully wrap mineral powder and cement particle surface. In this way, glue powder is prone to form a net at a low dosage, thus better inhibiting formation and expansion of crack. The combined action of the two aspects can not only improve efficiency of glue powder and mineral powder, but also enhance impervious performance of waterproof polymer cement mortar of low polymer-cement ratio. Beyond that, as average particle size of microsilica is only 1% of that of cement, microsilica added in cement mortar will fill cement particle void to make mortar more compact. Microsilica will combine with free Ca(OH)$_2$ to form a stable hydrate of calcium silicate (2CaO•SiO$_2$•nH$_2$O), thus improving impermeability. Table 2 shows the relationship between its dosage and impermeability pressure of mortar.

Table 2. the relationship between volume of microsilica addition and impermeability pressure of mortar

| Volume of addition (%) | 0   | 0.5 | 1   | 2   | 3   |
|------------------------|-----|-----|-----|-----|-----|
| Impermeability pressure /MPa | 7d  | 0.4 | 0.6 | 1.0 | 1.2 | 0.8 |
|                         | 28d | 0.6 | 1.0 | 1.5 | 2.1 | 1.2 |
According to Table 2, if microsilica dosage is 1%-2%, 7d and 28d impermeability pressure of polymer waterproof mortar can meet JC/T984-2005 standard, so microsilica is selected as waterproof mortar reinforcing material.

2.2. Selection and application of aggregate

In order to lower cost and further improve crack resistance and cold & heat cycle resistance performance of mortar, natural sand and mine tailings are selected as graded sand for preparing polymer waterproof mortar. Mine tailing is a kind of solid waste generated during mining and mineral separation, which is randomly discharged, leading to serious pollution on ecological environment. Therefore, by replacing mine tailings with natural sand in producing polymer waterproof mortar and other types of dry-mixed mortar products, excavation volume of natural sand will be reduced, river course and land protected, environmental and resource better conserved and product cost greatly reduced. Table 3 shows the influence of mine tailings and natural sand mixture ratio on crack resistance and cold & heat cycle resistance performance of mortar.

Table 3. Influence of mine tailings-natural sand mixture ratio on crack resistance and cold & heat cycle resistance performance of mortar

| SN | Cement /kg | Microsilica /kg | Admixture /kg | Fiber /kg | Mine tailings /kg | Natural fine sand/kg | Crack resistance | Cold-heat cycle resistance (10 cycles) |
|----|------------|-----------------|--------------|-----------|-----------------|---------------------|------------------|---------------------------------------|
| 1  | 420        | 22              | 18           | 40        | 150             | 350                 | Good            | Blistered and cracked                  |
| 2  | 420        | 22              | 18           | 40        | 200             | 300                 | Good            | Blistered and cracked                  |
| 3  | 420        | 22              | 18           | 40        | 250             | 250                 | Good            | No blistering and crack                |
| 4  | 420        | 22              | 18           | 40        | 300             | 200                 | Weak            | No blistering and crack                |

According to Table 3, under the same condition, mortar performs well in crack resistance and cold & heat cycle resistance if mine tailings/natural fine sand ratio is 1:1, the reason is that nearly spherical natural sand particle has "ball bearing" effect, surface area/volume ratio of spheroidal particle is small, cement mortar required to wrap particle is also small, and the remaining cement mortar is sufficient to enhance constructability of coating; polygonal mine tailings have mechanically interlocked particle surface, internal friction is thus increased and constructability of mortar is degraded. However, stone powder in mine tailings can fill voids, wrap sand particle surface and reduce internal resistance between aggregates, thus enhancing mortar workability, compactness and cold & heat cycle resistance.

2.3. Selection of anti-crack fiber

Considering thickness requirement for waterproof mortar during construction, grading of aggregate shall be adjusted to prevent mortar from cracking during drying process. Besides, a certain amount of anti-crack fiber shall be added to improve initial dry cracking-resistance of coating. Commonly used fibers and their performances are summarized in Table 4.

Table 4. Types and performance of commonly used fiber

| Items            | Function                                |
|------------------|-----------------------------------------|
| Wood fiber       | Good dispersibility but moderate crack resistance |
| Polypropylene fiber | Good dispersibility and crack resistance |
| Wollastonite fiber | Good dispersibility but poor crack resistance |
Based on crack resistance test (test temperature: 32-36°C, wind speed level: 2-4, air humidity: 40-55%), a mixture of wood fiber and polypropylene fiber is selected as anti-crack material for its performance in crack resistance.

2.4. Selection of water retention agent
Waterproof mortar shall have good water retention property and appropriate operable time to ensure that cement in the system contains sufficient amount of water of hydration to improve mortar strength, and shall also have appropriate setting time to guarantee sufficient operable time. Therefore, different types and performances of water retention agents are of importance to physical property and workability of waterproof mortar. Main types of water retention agents include cellulose derivative, starch ether, bentonite, etc. Water retention rates of different water retention agents are measured utilizing vacuum suction method at differential pressure of 400±5mm mercury column, and draft filtering time is 30min.

| Water retention agent | HPMC | MC-1 | MC-2 | Starch ether | Bentonite |
|-----------------------|------|------|------|--------------|-----------|
| Water-retention rate (%) |     |      |      |              |           |
| HPMC                  | 95.1 | 95.3 | 94.1 | 88           | 80        |

According to Table 5, MC-1 (viscosity: 30000CP) is selected as water retention agent of polymer waterproof mortar for its high water-retention rate.

2.5. Selection of other addition agents
A proper amount of super-plasticizer shall be added to reduce water consumption of waterproof mortar and minimize the formation of pore; a proper amount of early strength admixture shall be added to enhance early strength of waterproof mortar.

3. Results and discussions
Based on systematic study and test on raw materials of polymer waterproof mortar, cost-effective dry powder polymer waterproof mortar is developed, and all its performance indexes are proved to meet the standard of Polymer Modified Cement Mortars for Waterproof (JC/T984-2005) upon inspection by Beijing Building Materials Quality Supervision and Testing Station, and the following conclusions are summarized:

(a) If polymer-cement ratio is 0.06-0.1, the application of re-dispersible glue-powder will significantly improve cohesive strength and flexibility of mortar and reduce ratio of compressive strength to flexural strength.

(b) Rationally graded mine tailings and natural sand contribute greatly to better performance of waterproof mortar in crack resistance and cold & heat cycle resistance. Stone powder in mine tailings fills pores in coating, thus making mortar more compact and anti-permeable.

(c) Thanks to the synergy effect of microsilica and glue powder, waterproof and anti-permeability of polymer waterproof mortar is improved; a mixture of microsilica and cement can improve water-resisting strength and crack resistance of mortar.

(d) Water retention agent, if utilized rationally, can change thixotropy, water retention property and constructability of polymer waterproof mortar. Low viscosity MC performs well on this regard.

(e) Different types and dosages of anti-crack materials will lead to different dry cracking-resistance performances of waterproof mortar; 1mm long wood fiber and 6mm polypropylene fiber are commonly used in a combined way. Besides, water reducing agent is added to decrease water consumption of mortar and minimize the number of pore.

4. References
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