Recent Research and Development of Polymer-Modified Mortar and Concrete in Japan

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Abstract

The present paper deals with the recent research and development activities of polymer-modified mortar and concrete in the Japanese construction industry. In Japan, the active research and development of the polymer-modified mortar and concrete have been carried out for the past about 50 years, and they are currently used as dominant construction materials in various applications because of their high performance, multifunctionality and sustainability compared to conventional cement mortar and concrete. The recent research and development activities of the polymer-modified mortar and concrete are concerned with repair systems for deteriorated reinforced concrete structures, strengthening (or retrofitting) methods and exfoliation (or delamination) prevention methods for existing reinforced concrete structures, liquid-applied membrane waterproofing systems, advanced polymeric admixtures such as high-grade redispersible polymer powders and hardener-free epoxy resins, intelligent repair materials, application of accelerated curings, semiflexible pavements, and drainage pavements with photocatalyst.

INTRODUCTION

In Japan, the active research and development of polymer-modified mortar and concrete have been performed for the past about 50 years, and they are currently used as popular construction materials in various applications because of their high performance, multifunctionality and sustainability compared to conventional cement mortar and concrete. The polymer-modified mortar and concrete certainly come within the category of environment-conscious or sustainable construction materials, considering the growing recognition of the saving of natural resources, the longevity of infrastructures and the protection of natural environment. The research and development of the polymer-modified mortar and concrete proceed actively with a great interest in Japan at present. The present paper reviews the important and interesting topics in the recent research and development activities of the polymer-modified mortar and concrete in the Japanese construction industry for the past several years.
GENERAL TRENDS IN RESEARCH AND DEVELOPMENT ACTIVITIES

In the Japanese construction industry, polymer-modified mortar and concrete which are made by using polymeric admixtures were developed in the early 1950s, and became the dominant construction materials in the late 1960s. Commercially available polymeric admixtures in Japan are classified into polymer dispersions, redispersible polymer powders, water-soluble polymers and liquid polymers. The polymeric admixtures widely used at present are polymer dispersions such as styrene-butadiene rubber (SBR) latex, poly(ethylene-vinyl acetate) (EVA) and polyacrylic ester (PAE) emulsions, and redispersible polymer powders such as poly (vinyl acetate-vinyl versatate-acrylic ester)(VA/VeoVa/AE), poly(ethylene-vinyl acetate) (EVA) and poly(vinyl acetate-vinyl versatate) (VA/VeoVa) powders. The polymer-modified mortar is most widely used for repair and finish works, but the polymer-modified concrete is employed only in limited applications.

REPAIR SYSTEMS FOR DETERIORATED REINFORCED CONCRETE STRUCTURES

In Japan, the early deterioration of reinforced concrete structures has become a big social problem in recent years. In the construction industry, the development of effective repair materials and their execution systems comes to an increasingly important issue from the viewpoint of the longevity of infrastructures at present. Repair materials for the deteriorated reinforced concrete structures include impregnants for concrete quality modification and improvement, corrosion-inhibiting coating materials for reinforcing bars, patch materials, surface preparation materials, coating materials for finish and protection, and grouts for concrete cracks. Figure 1 illustrates the typical application or execution systems of the repair materials using polymer-modified pastes and mortars for deteriorated reinforced concrete structures. The corrosion-inhibiting coating materials using polymer-modified pastes such as SBR-, PAE- and VA/VeoVa/AE-modified pastes containing corrosion inhibitors, e.g., calcium nitrite and lithium nitrite are used for the treatment of the reinforcing bars. The patch materials are employed for the back filling of the damaged portions of the concrete. Shotcrete systems using such materials are applied for repair work with large areas (Hayakawa et al., 2005), (Yokoyama et al., 2005).

The important quality requirements for the patch materials are as follows: (1) Good adhesion or bond to the concrete substrates, (2) Long-term durability or weatherability, (3) Almost the same elastic modulus and coefficient of thermal expansion as the concrete, and (4) Good dimensional stability (small drying shrinkage). Most polymer-modified mortars using polymer dispersions such as SBR and chloroprene rubber (CR) latexes, EVA, VA/VeoVa and PAE emulsions, and redispersible polymer powders such as EVA, VA/VeoVa, PAE and VA/VeoVa/AE powders meet the above quality requirements for the patch materials. In recent years, the adhesion or bond (to the concrete substrates) (Yamabe et al., 2001), and long-term durability (Park et al., 2005), (Inoue et al., 2005), (Makishima and Uomoto, 2006) of the polymer-modified mortars for the patch materials have actively been investigated with an increase in the demand for such polymer-modified mortars. Surface preparation materials and coating materials for finish and protection are applied on surfaces after the patch work. The polymer-modified mortars or pastes with special mix design are generally used for such materials. Polymer-modified pastes or slurries are also applied for grouting cracks with widths of 1.0mm or more on the concrete substrates.
STRENGTHENING OR RETROFITTING METHODS FOR EXISTING REINFORCED CONCRETE STRUCTURES

Existing reinforced concrete structures such as slabs and beams (or girders) have often been strengthened with overlays to increase their thickness (or depth) by the troweling or shortcreting work of polymer-modified mortars on the bottom surfaces of the slabs and beams (or girders) (Satoh and Kodama, 2003). Figure 2 represents the concept of the additional thickness (or depth) overlay strengthening methods using the polymer-modified mortars. Existing reinforced concrete columns and shear walls have recently been retrofitted with the troweling or shortcreting work of polymer-modified mortars for seismic strengthening methods (Miyauachi and Kuroishi, 2005), (Sugiyama et al., 2005). The application of the seismic strengthening methods provides a good shear reinforcement effect, and markedly improves the seismic performance of the existing reinforced concrete structures.

ADHESIVES OR BONDING AGENTS FOR EXFOLIATION (OR DELAMINATION) PREVENTION METHODS

In Japan, the exfoliation (or delamination) of concrete lumps due to the deterioration of reinforced concrete structures has recently caused serious accidents, and become a big problem in the construction industry. Most conventional exfoliation (or delamination) prevention methods are applied to the reinforced concrete structures by the externally bonding of continuous organic or inorganic fiber sheets with epoxy resin-, acrylic resin- and rubber-based adhesives or bonding agents to the concrete substrates. The disadvantages of the conventional exfoliation (or delimitation) prevention methods are poor adhesion to the concrete substrates due to moisture in concrete and the apprehensive weatherability due to the degradation of the polymeric adhesives or bonding agents. To overcome such disadvantages, new exfoliation (or delamination) prevention methods using polymer-modified pastes and mortars for adhesives or bonding agents with vinylon (Ido et al. 2003), aramid, (Ido et al. 2003), polyethylene (Tanimoto et al., 2004) and alkali-resistant glass fiber sheets (Takeuchi and Sugiyama, 2005) in recent years. Figure 3 shows the concept of the new exfoliation or delamination prevention methods using the polymer-modified pastes and mortars. The great advantage of the new methods is easy application to wet concrete substrates.

LIQUID-APPLIED MEMBRANE WATERPROOFING SYSTEMS

In comparison with conventional membrane waterproofing systems such as asphalt membrane waterproofing systems and liquid-applied membrane waterproofing systems with organic solvents, liquid-applied membrane waterproofing systems using polymer-modified mortars or slurries are free from poisonous organic solvents or gases with disagreeable odors, and do not pollute the atmosphere. The waterproofing systems are also called “polymer-modified cement (cementitious) membrane waterproofing systems”. Figure 4 exhibits the standard execution procedures for the polymer-modified cement membrane waterproofing systems. In general, the polymer-modified mortars or slurries for the polymer-modified cement membrane waterproofing systems are prepared at polymer-cement ratios of 20 to 300% by using PAE and EVA emulsions or SBR latex, and have tensile strengths of 0.7 to 8.0MPa, elongations of 25 to 400% and adhesions to the concrete substrates of 0.75 to 2.8MPa as waterproofing membranes (Hayashi et al., 2002). In Japan, the polymer-modified cement membrane waterproofing systems are annually used in new construction work of ca. 4.0 million m^2 (ca. 8180t) and in repair work of ca. 3.3 million m^2 (ca. 7350t)
for deck roofs, verandas, reservoirs, underground interior and exterior walls (Tsuchida et al., 2002).

HIGH-GRADE REDISPERSIBLE POLYMER POWDERS

In recent years, the quality of redispersible polymer powders has markedly been improved, in particular, in their film formation characteristics, and the properties of polymer-modified mortars using the redispersible polymer powders have become similar to those of polymer-modified mortars using polymer dispersions. As a result, in the manufacture of polymer-modified mortar products, the replacement of polymer dispersions by the high-grade redispersible polymer powders, i.e., the change of two-packaged systems to one-packaged systems is promoted in Japan. Commercial high-grade redispersible polymer powders are EVA, PAE, poly(styrene-acrylic ester)(SAE), VA/VeoVa and VA/VeoVa/AE powders. The merits of the one-packaged polymer-modified mortar products using the high-grade redispersible polymer powders are as follows: (1) Manufacture of high-quality polymer-modified mortars due to the holding of precise mix proportions by factory production, (2) High productivity of polymer-modified mortars due to rational materials handling, mixing and execution procedures on the basis of the incorporation of mixing water only on job site, (3) As derived from (2), a reduction in construction cost due to possible easy construction management and short construction period, and (4) Reduced wastes such as metal and plastics cans on job site due to the uses of paper bags only, silos for storage and containers for transportation. The polymer-modified mortars using the redispersible polymer powders are used in the fields of coating materials for textured finishes, surface preparation materials for coatings, self-leveling materials, tile adhesives and repair materials. The author’s group has developed a poly(oxyethylene)-poly(oxypropylene)-monooleylether-based antifoamer and a polyethylene glycol-based shrinkage-reducing agent to improve the relatively large air content and drying shrinkage of the polymer-modified mortars using the redispersible polymer powders (Ohama and Matsumoto, 2003).

INTELLIGENT REPAIR MATERIALS

Hardener-Free Epoxy-Modified Mortars with Autohealing or Self-Repairing Function

Conventional epoxy-modified mortars and concretes have an inferior applicability due to the two-component mixing of the epoxy resin and hardener, the toxicity of hardeners such as polyamine and polyamide and the obstruction of cement hydration by the hardeners. The author’s group found out that even without any hardeners the epoxy resin can harden in the presence of the alkalis or hydroxide ions produced by the hydration of cement in the epoxy-modified mortars as expressed by the following formula (Ohama et al., 1992).

This means the development of the epoxy-hydraulic cement systems of new concept. In hardener-free epoxy-modified mortars with polymer-cement ratios of 20% or less, the hardening degree of the epoxy resin is 50 to 90% (Ohama et al., 1995), and unhardened epoxy resin exists. It is considered that the unhardened epoxy resin may be sealed with hardened epoxy resin phase in the epoxy-modified mortars. The epoxy resin phase forms self-capsuled epoxy resin. The self-capsuled epoxy resin can be broken under loading in the epoxy-modified mortars, and the unhardened epoxy resin in the self-capsuled epoxy resin may fill microcracks in the mortars after loading. Then the unhardened epoxy resin filling the microcracks may harden by hydroxide ions in the mortars. Therefore, the microcracks are autohealed or self-repaired with the
epoxy resin in the epoxy-modified mortars (Ohama et al. 2001). The same system can be applied to hardener-free epoxy-modified concretes. Figure 5 shows the simplified model for the autohealing or self-repairing mechanism of the microcracks in the hardener-free epoxy-modified mortar and concrete. Such hardener-free epoxy-modified mortars and concretes have a autohealing or self-repairing function for the microcracks, and may be intelligent materials.

**Polymer-Modified Mortars with Nitrite-Type Hydrocalumite**

Nitrite-type hydrocalumite \([3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca(NO}_2)_2 \cdot n\text{H}_2\text{O} \ (n=11\sim12)]\) is a corrosion-inhibiting admixture or anticorrosive admixture which can adsorb the chloride ions (Cl\(^{-}\)) causing the corrosion of reinforcing bars and liberate the nitrite ions (NO\(_2^\cdot\)) inhibiting the corrosion as expressed by the following formula, and provides excellent corrosion-inhibiting property to the reinforcing bars in reinforced concrete (Tatematsu and Sasaki, 2000). Figure 6 illustrates the chloride ions adsorption mechanism of the nitrite-type hydrocalumite in reinforced concrete. Polymer-modified mortars using polymer dispersions and redispersible polymer powders with the nitrite-type hydrocalumite (calumite) have superior corrosion-inhibiting property and durability, and attract notice as effective repair materials for deteriorated reinforced concrete structures (Ohama et al. 2006). Figure 7 represents the calumite content vs. the corrosion rate of the reinforcing bars embedded in the polymer-modified mortars with the calumite. The calumite contents of around 5 to 10\% are recommended to make effective repair materials for deteriorated reinforced concrete structures (Ohama et al., 2006).

**APPLICATION OF ACCELERATED CURINGS**

The application of autoclave curing(180\(^\circ\)C and 1.01MPa in pressure) to polymer-modified mortars and concretes has not been conducted till now because of possible thermal degradation of polymers in them during the autoclave curing. The application of the autoclave curing to SBR-modified concrete with a slag content of 40\% and a polymer-binder ratio of 20\% provides about three times higher tensile strength and twice higher compressive strength than unmodified concrete (ordinary cement concrete) (Joo et al., 2004). Accordingly, the autoclave curing can be applied to SBR-modified concretes using slag for precast products. The feasibility study to examine hardener-free epoxy resin as a polymeric admixture for the accelerated curing of cement concrete shows that the application of a 120\(^\circ\)C-autoclave curing or 90 \(^\circ\)C–steam curing plus 120 \(^\circ\)C–heat curing to hardener-free epoxy modified mortars with polymer-cement ratios of 10 to 20\% develops about twice to three times higher flexural strength and about twice higher compressive strength than unmodified mortar(ordinary cement mortar)(Ohama and Takahashi, 2003).
PAVEMENT APPLICATIONS

Semiflexible pavements are executed by grouting the voids of open-graded asphalt concretes with polymer-modified pastes or slurries. The pavements are applied to heavy traffic roads, intersection pavements, bus stops, parking lots and airport runways because of their excellent rutting resistance, load spreadability, abrasion resistance, oil resistance and colorability (Uematsu et al., 1991). The drainage pavements coated with polymer-modified pastes containing photocatalyst (anatase-type titanium dioxide) have recently been developed to effectively decompose car exhaust gases with nitrogen oxides on road surfaces by the action of the photocatalyst and prevent air pollution (Ishimori et al., 2000). The pavements have high abrasion resistance to car traffic, and therefore semipermanently hold their air purification function.

CONCLUSIONS

In Japan, recent technical innovations in the construction industry have brought about the active research and development of polymer-modified mortar and concrete as high-performance and multifunctional construction materials. From the viewpoint of sustainable development in the construction industry, environment-conscious polymer-modified mortar and concrete have been developed with a great interest in recent years. The polymer-modified mortar and concrete with high performance, multifunctionality and sustainability are expected to become the promising construction materials in Japan in the 21st century.

REFERENCES


Figure 1  Typical application or execution systems of repair materials using polymer-modified pastes and mortars for deteriorated reinforced concrete structures.

Figure 2  Concept of additional thickness (or depth) overlay strengthening methods using polymer-modified mortars.

Figure 3  Concept of new exfoliation or delamination prevention methods using polymer-modified pastes and mortars.
Figure 4  Standard execution procedures for polymer-modified cement membrane waterproofing systems.

Figure 5  Simplified model for autohealing or self-repairing mechanism of microcracks in hardener-free epoxy-modified mortar and concrete.
3CaO Al₂O₃ Ca(NO₂)₂ nH₂O+2Cl⁻ → 3CaO Al₂O₃ CaCl₂ nH₂O+2NO₂⁻
(Nitrite-type Hydrocalumite)
(adsorb) (liberate)

Cl⁻ : Chloride Ions
NO₂⁻ : Nitrite Ions
★ : Nitrite-type Hydrocalumite
Red: Corrosion Inhibition Area by Nitrite Ions

Figure 6 Chloride ions adsorption mechanism of nitrite-type hydrocalumite in reinforced concrete.

Figure 7 Calumite content vs. corrosion rate of reinforcing bars embedded in polymer-modified mortars with calumite.