An investigation on the microstructure formation of polymer modified mortars in the presence of polyacrylate latex

Ye TIAN\(^1\), Zong-jin LI\(^2\), Hong-yan MA\(^2\), Xian-yu JIN\(^1\), Nan-guo JIN\(^1\)

\(^1\) Zhejiang University, Hangzhou, China
\(^2\) Hong Kong University of Science and Technology, Hong Kong, China

ABSTRACT: In this research, the microstructure formation of polyacrylate (PA) latex modified mortars was investigated from mixing to hardening. The polymer film forming process was studied, with specific emphasis on the chemical and physical reactions between polymer and cement hydration products. An improved four-step model was proposed for representing the mechanism of polymer modification in view of the reactivity of polymer latex in cement-based materials. And the influence of PA latex on the microstructure formation of mortars was revealed through the analysis of pore structure and polymer distribution. Owing to cement hydration, the uniform dispersion of polyacrylate polymer in fresh mortar will be destructed, and polymer particles will deposit and flocculate into big groups at some local positions. The modification of polyacrylate polymer on cement-based materials is localized which can be stated as the localization of polymer modification. The addition of PA latex will also introduce some air voids into mortars due to the chemical reaction between its surfactant and cement hydrates. This is important for the physical and mechanical properties improvement because a kind of purposefully designed polymer latex will effectively enhance the performance of cement-based materials in a relative small dosage, which means cutting the cost down and broadening its application.

1 GENERAL INSTRUCTIONS

Cement-based materials have now become the dominant construction materials for the civil infrastructure all over the world. The addition of a minor amount of polymer into a cement mix can significantly enhance the properties of the resulting material, which is known as a polymer modified cement-based material (Chung, 2004). In polymer modified cement-based material, polymer particles, unhydrated cement particles and cement hydration products will form a polymer-cement co-matrix together (Ollitrault-Fichet et al., 1998). The presence of the polymer particles will refine the pore structure, thereby decrease the porosity (Liu et al., 2003). Moreover, the polymer modified cement-based materials show a good workability and enhanced water retention. And, mechanically, the presence of polymer tends to increase the flexural strength and toughness (Sujjavanich and Lundy, 1998; Zhong and Chen, 2002). Owing to these superior properties, the polymer modified cement-based materials have already been widely used as the adhesive or finishing materials, and repair materials for reinforced concrete structures.

Due to the rising importance of polymer modified cement-based materials in civil construction, many attempts have been made to clarify the mechanism of polymer modification (Sakai and Sugita, 1995; Su et al., 1996; Afridi et al., 2003; Wang et al., 2006). Among these researches, Ohama’s three-step model is taken as the most representative achievement in describing the formation of the polymer-cement co-matrix (Ohama, 1995). According to Ohama, the polymer
particles firstly uniformly disperse in the cement paste. And the polymer particles deposit partially on the surfaces of the cement particles. As the cement hydration proceeds and the capillary water is consumed, the polymer particles flocculate to form a continuous close-packed layer on the surfaces of the cement-gel-unhydrated-cement particles mixtures. Finally, the close-packed polymer particles on the cement hydrates coalesce into continuous films, and the films bind the cement hydrates together to form a monolithic network in which the polymer phase interpenetrates throughout the cement hydrates phase. Taking Ohama’s model as a research base, some adjustments and refinements, in addition with several experimental works, are made to established an integrated model in which the reciprocal influences between the polymer and the cement particles are incorporated and implemented on a time scale (Beeldens et al., 2005; Gemert et al., 2005).

However, in Ohama’s model, a continuous polymer film or an interpenetrative polymer network is indispensable for an effective modification and properties improvement of the polymer modified cement-based materials. But sometimes in cement-based materials, only scattered polymer films are found, especially for the polymer modified cement-based materials with a low polymer/cement (P/C) ratio (Afridi et al., 2003; Wang et al., 2005;). While the addition of small amounts of polymers (usually below 4%) also clearly influences the properties of the hardened materials. It is clear that there exist other morphologies of polymer materials other than continuous polymer films, and also other mechanisms of polymer modification, in a low P/C ratio.

In this research, newly developed polyacrylate (PA) latex was used as the polymer admixture. A series of tests were carried out to simulate the chemical and physical reactions happened between polymer latex and cement particles in polymer modified mortars from mixing to hardening. The morphologies of the co-matrix were analyzed and identified. And a new model expanded from Ohama’s research on the mechanism of polymer modification was proposed based on the Scanning Electronic Microscope (SEM) and Energy dispersive X-ray detector (EDX) observations.

2 MATERIALS AND SAMPLES PREPARATION

2.1 Polyacrylate latex

The PA latex used in this research is a kind of milky suspension which is stabilized by surfactant, sodium dodecyl sulfate (SDS). The diameter of PA particles ranges from 40nm to 200nm. And the mean diameter of PA particles is 80.2 nm.

The molecule structure of PA is composed of a main chain and thousands of short side chains which can be classified according to their hydrophilic properties as anionic and nonionic. EDX analysis of PA polymer film states that its carbon/oxygen (C/O) ratio ranges from 1.5 to 3. While in concrete, the cement hydration products are all inorganic with C/O ratio close to 0. Even the carbonation of cement can only generate the chemical reaction products with the C/O ratio of 0.33 (CaCO₃) which is much lower than that of PA polymer. So the value of C/O ratio, in this research, will be used to identify the trace of polymer modification in concrete.

2.2 Other raw materials

Ordinary Portland cement (ASTM type I), with the density of 3.15 g/cm³, was used in this study. The Blain specific area of cement is 3.85×10³ cm²/g. And the average particle size of Portland cement is 18.09μm. The size of quartz sand employed in this research ranges from 0.5mm to 3.1mm. The fineness modulus and relative density of quartz sand are 1.6 and 2.66 respectively. A milky alkali-resisting silicone antifoaming agent for concrete was applied to reduce the entrainment caused by the residual SDS in PA latex. The deionized water was used in this study.
2.3 Mix proportions and samples preparation

Three kinds of PA modified mortars were employed in this research to investigate the mechanism of PA latex modification on cement-based materials. All mortar samples were prepared with a water/cement ratio of 0.5 and a sand/cement ratio of 2. Samples PA00, PA05 and PA10 represent the mortars with the P/C ratio of 0.00, 0.05 and 0.10, respectively. For the mortars modified with PA latex, 0.5% defoamer was added by weight of cement. All the samples were cured in standard curing conditions (95%RH and 25°C) for 3 days and a nature curing at ambient humidity and temperature (60%RH and 20°C) from 3d to 28d.

3 TEST METHODS

3.1 Adsorption ratio analysis

The adsorption ratio analysis will show us the initial state and movement of PA particles in cement mixture just after mixing. The adsorption of PA particles on the surface of cement particles and sand was evaluated with total organic carbon (TOC) content analysis. PA latex was mixed with cement with P/C ratio of 0.05, 0.10, 0.20, 0.50 and 1.00, respectively. And P/S (polymer/sand) ratio of 0.05, 0.10 and 0.50 was applied in this test. Using a TOC-5000A analyzer, the adsorption ratio of PA particles can be calculated with the TOC in diluted pure PA latex and in each diluted suspension.

3.2 Simulation test

The simulation test was carried out to give a visualized demonstration of the chemical and physical reactions between PA latex and cement in pore solution of PA polymer modified mortars during cement hydration. All the simulation tests were performed in a glass tube. In the test, PA latex was mixed with cement in different weight ratio. And the mixture was diluted into 20 ml with deionized water. Then the mixture was carefully preserved until the mixture got to a stable situation.

3.3 Mercury intrusion porosimetry (MIP) test

The mercury intrusion test was conducted with a Micromeritics AutoPore IV 9500 MIP. The concrete samples were collected from the crushed mortar samples at 12h, 18h, 1d, 3d, 7d and 28d.

3.4 SEM and EDX observations

To clarify the morphologies of polymer-cement co-matrix in PA latex modified mortars, SEM and EDX observations were performed to characterize the samples collected from simulation test and crashed mature PA modified mortars using a JEOL-6300F SEM. All samples were treated with 0.1M/L HCl.

4 TEST RESULTS AND DISCUSSIONS

4.1 Adsorption of PA polymer on cement particles and sands

It is generally accepted that the polymer particles will uniformly disperse in the solution of fresh cement mortar. As cement particles are much bigger than polymer particles, there is a good chance that a moving polymer particle in fresh mortar will hit a cement particle and adhere on the surface of it. And this procedure is believed to be driven by physical forces more than chemical ones. But in comparison with the circumstance conditions in latex suspension, the
polymer particles in water phase of mortar will face a strong alkaline and ionic attack due to the hydration of cement. The broken stabilities will, undoubtedly, challenge the uniform dispersion of PA particles in fresh cement mortars.

Just as shown in Figure 1, 88.65% PA polymer particles are adsorbed on the surface of cement particles when P/C ratio is 0.05. This phenomenon indicates that considerable PA particles will assemble and deposit on the surface of cement particles, especially in a low P/C ratio. As pointed out by Atahan et al., the carboxylate group, -COO-, will react with calcium ion to form a precipitate with a very low solubility (Atahan et al., 2008). So carboxylate groups on PA polymer particles can be linked by calcium ions with strong chemical bonds. During cement hydration, cement particles will release a large number of calcium ions into solution, so a lot of PA particles will be attracted on the surface of cement particles. But when PA particles envelope the cement particles entirely, no more PA particles will be absorbed. So the adsorption ratio, as shown in Figure 1, drops rapidly when P/C ratio increases. In comparison with absorption ratio of PA particles on cement, the absorption ratio on sand is much lower. As demonstrated in Figure 2, only 2.58% PA particles adhere on sand when polymer/sand (P/S) ratio gets to 0.05. It is because sand will not release any ions into pore solution. Only physical adhesion force exists between PA particles and sand rather than strong chemical bonds.

It can be concluded from this research that the absorption ratio, \( P_{ad} \), is negative exponential related with P/C or P/S ratio, which can be represented as:

\[
P_{ad} = a \cdot \exp\left(-\frac{r}{b}\right) - c
\]

where \( a, b \) and \( c \) are experiment constants, \( r \) is P/C ratio or P/S ratio.

4.2 Simulation test results

As indicated by Figure 1 and Figure 2, there will still be a part of PA polymer particles left in the pore solution of cement-based materials. In ohaµaµ’s model, this part of polymer particles will disperse uniformly in cement solution and finally be buried in cement hydration products forming a kind of organic-inorganic compounds.

While in this research, the surfactant, SDS, in PA latex will react with calcium ions forming most likely CaSO\(_4\) and CaSO\(_4\cdot2H_2O\) which will soon settle from cement solution (Atahan et al., 2008). The uniform dispersion of PA particles in cement pore solution will also be broken due to the sediment of SDS. As shown in Figure 3, the stable mixture PA latex and cement will separate into 4 layers: the supernatant liquid layer, the flocculation layer, the coagulation layer, and the cement-PA compound layer. A detailed demonstration of the layered structure is shown in Figure 4. The P/C ratios of the mixtures in Figure 3, from left to right, are 0.2, 0.4, 0.7 and 1.0, respectively. It can be concluded from Figure 3 that, with the increase of P/C ratio, the heights of each layer change a lot which means that PA polymer particles will not disperse uniformly in cement pore solution. The physical grouping of PA particles, as well as the
chemical reactions between PA particles and cement hydration products, will form different types of co-matrixes. The difference between the co-matrixes, such as density, will cause the separation and isolation which leads to the multi-layering of the mixture.

![Figure 3: Mixture of PA latex and cement](image)

![Figure 4: Multi-layered structure of the mixture](image)

4.3 Pore Structure of PA Modified Mortars

The incremental pore volume of PA modified and unmodified mortars are plotted against pore diameter in Figure 5-7. As shown in Figure 5-7, the pore structure of PA latex modified mortars is much different from the unmodified mortar. At different ages, only one main peak appears in the curves of PA00 with a bandwidth ranging from 0.2μm to 3μm. While the curve peak moves toward to smaller diameter with the addition of PA latex. The curve peaks of PA05 and PA10 site from 0.01μm to 1μm. At the same time, another curve peak emerges with the pore diameter ranging from 10μm to 100μm. So the pore structure of PA modified mortars at different ages, unlike the unmodified one, can be outlined as a saddle-like or double peaked curve.

Because the mean diameter of PA particles is much lower than that of cement particles. So the left peak of PA modified mortars can be attributed to the filling effect of PA particles. PA particles will fill the mortar pores and shift the curve peak form bigger diameters to smaller diameters. The other peak can be explained as the air introduction effect due to C_{12}H_{25}SO_{3}Na, which is the emulsifier during PA manufacture. So PA latex addition will cause two contrary results. On one hand, PA particles will refine the pores in PA latex modified mortars. On the other hand, PA latex modification will introduce additional large diameter pores in mortars. Generally, as shown in Figure 8, the porosity of PA modified mortars increase with the increase of P/C ratio.

![Figure 5: Pore structure of PA00](image)

![Figure 6: Pore structure of PA05](image)

![Figure 7: Pore structure of PA10](image)

![Figure 8: Porosity of mortars](image)
4.4 SEM and EDX observations

As demonstrated in Figure 9, after acid etching, the microstructure of unmodified mortar, PA00, is loosely packed. The holes and caverns in etched PA00 represent the acid corrosion and decomposition of cement hydration products. While for PA10, several pieces of flattened films can be clearly recognized covering the cement hydrates. So the cement hydration products are all well protected by the chemical resistance of flattened films. But it is obvious that the flattened films are not well connected. The EDX analysis on the matrix, as shown in Table 1, states that few carbon atoms can be detected in etched PA00. It proves that acid treatment will effectively remove the carbon element from cement mortars. But after acid etching, there are still considerable carbon content left in PA10. The C/O ratio of PA10 is much higher than PA00 and close to pure PA film. It indicates that flattened film is mainly composed of PA polymer. Besides carbon and oxygen, calcium and silicon are also detected in PA10. As calcium and silicon are the key elements consisting cement hydration products, so the flattened film in PA10 is a compound of PA film and cement hydrates.

![PA00](image1) ![PA10](image2)

Figure 9 Microstructure of PA modified mortars after acid etching

<table>
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<th>Mix</th>
<th>Elements</th>
<th>C</th>
<th>O</th>
<th>Ca</th>
<th>Si</th>
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<td>34.72%</td>
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<td>0.00%</td>
<td>0.00%</td>
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</tr>
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</table>

5 MECHANISM OF PA POLYMER MODIFICATION

In this research, based on the adsorption test, simulation test, pore structure analysis and SEM analysis, an improved model is proposed based on Ohama’s investigation. PA polymer modification in cement can be divided into 4 steps, which is represented in Figure 10.

At the first step, polymer particles, cement, water, and sand are mixed together. This step is defined as the initial situation which means no chemical and physical reactions happen at this stage. So, as shown in Figure10 (a), polymer particles, cement particles and sands are all uniformly distributed in the mixture. Then, at the second step in Figure10 (b), initial cement hydration process is induced by the contact of cement and water. Considerable PA polymer particles will stick to cement particles due to chemical bonding, and stick to sand due to physical adherence. The released calcium ions will cause failure of surfactant, so polymer particles will group together randomly and disorderly. Because calcium ions usually concentrate around cement particles, polymer flocculation will generate in some local places in fresh mortar.
The following step is represented in Figure 10 (c). Although the packed polymer particles on the surface of cement particles will significantly retard cement hydration process. But finally, the cement hydrates will break through the envelope and tear up the surrounding polymer layer into pieces. With the progress of cement hydration, water phase in polymer flocculation will be dried out. At the same time, some cement hydration products may grow or embed in polymer flocculation. And polymer flocculation should partially coalesce into polymer film. The final step includes further cement hydration and film formation, as demonstrated in Figure 10 (d). With the consumption of water, polymer flocculation will be converted into film or polymer-cement hydrates co-matrix completely. Because polymer flocculation will not distribute uniformly in fresh mortar, the film or co-matrix may concentrate in some local places in hardened mortar accordingly. This phenomenon can be named as the localization of polymer modification.

![Diagram](image)

Figure 10 Modeling of PA polymer modification in cement-based materials

6 CONCLUSIONS

In this research, the microstructure formation process of PA modified mortar was investigated. An improved four-step model was proposed to represent the mechanism of PA latex modification on cement mortar. Following conclusions can be drawn.

1. After mixing, PA particles will not uniformly distribute in fresh mortar due to the chemical bonding with calcium ions which are released by cement particles. And part of PA particles will adhere on the surface of sand.

2. Polymer emulsifier in PA latex will lose its activity in cement mortar. The sedimentation of polymer emulsifier will cause the flocculation of PA polymer particles in solution.

3. In macro-level, PA latex addition will fill and refine the pores of mortars and, at the same time, induce big pores to mortars.

4. A kind of polymer-cement hydrates compound can be recognized in PA modified mortars.

7 ACKNOWLEDGEMENT

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8 \hspace{0.5em} \textbf{REFERENCE}


