Effects of Two Redispersible Polymer Powders on Efflorescence of Portland Cement-based Decorative Mortar

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The effects of redispersible polymer powders of ethylene/Vinyl acetate copolymer (EVA) and ethylene/vinyl laurate/vinyl chloride terpolymer (E/VL/VC) on the efflorescence of Portland cement-based decorative mortar (PCBDM) were studied. The results showed that EVA slightly prolongs the efflorescence duration of fresh PCBDM; and exacerbates efflorescence of hardened PCBDM, because it increases the content of soluble salts such as Ca\(^{2+}\), K\(^{+}\), Na\(^{+}\) ions in hardened PCBDM and promotes their migration. E/VL/VC exacerbates efflorescence of fresh PCBDM due to it easily dissolves in the surface water; but reduces efflorescence of hardened PCBDM, which is attributed to that it decreases the soluble salts content in hardened PCBDM and prohibits salts migration.

Keywords: portland cement-based decorative mortar (PCBDM), EVA, E/VL/VC, efflorescence, soluble salts.

1. INTRODUCTION

Portland cement-based decorative mortar (PCBDM) is especially suitable for the decoration of wall and has excellent match with the Exterior Insulation and Finish System (EIFS), due to its outstanding advantages, such as unique nature decorative effect, good weather resistance, breathing, and crack-resistance. But PCBDM has the common weakness of Portland cement-based materials — easy to occur efflorescence [1, 2]. The typical phase of efflorescence substance is calcium carbonate, which is formed by the reaction of calcium hydroxide and carbon acid; moreover, some soluble salts in mortar may also migrate to the surface and form efflorescence, such as sodium sulfate and potassium sulfate [3, 4].

Nowadays redispersible polymer powders are the popular organic binders to change the properties of dry-mix mortar, especially to improve adhesive strength due to the polymeric film formation inside the composite [5, 6]. Besides the ability to form film, according to some researchers [7–10], chemical interactions occur between polymers and Portland cement. The study of Silva D.A. [10] shows that the acetate groups of EVA copolymer undergo alkaline hydrolysis and interact with Ca\(^{2+}\) ions of the cement paste to form an organic salt (calcium acetate), and the calcium hydroxide content is decreased.

Both the film formation and chemical reactions influence the efflorescence forming in PCBDM, but few literatures reported about efflorescence of PCBDM modified with redispersible powders, especially with respect to the comparison of different co-and ter-polymers. In our former study [11, 12], Ethylene/vinyl acetate copolymer (EVA) reduces the primary efflorescence of PCBDM, but exacerbates the efflorescence of 1-day-old PCBDM; Ethylene-vinylchloride-vinyl laurate terpolymer (E/VL/VC), which is very popular for EIFS renderings, stuccos and grouts, offering a hydrophobic effect, exacerbates the efflorescence of fresh PCBDM. But the effects of EVA and E/VL/VC on efflorescence of PCBDM cured for longer ages and the mechanism have not been investigated. Therefore, in this paper, the efflorescence of fresh and hardened PCBDM modified with EVA or E/VL/VC was tested. In addition, the mechanisms were also explored by investigating two aspects: the efflorescence source such as the soluble salts and ions content, and the influencing factors of salts migration such as the surface topography and hydrophobility of PCBDM.

2. EXPERIMENTAL

2.1. Materials

52.5R white Portland cement, redispersible polymer powders (EVA and E/VL/VC), quartz sand, iron oxide red pigment, de-ionized water were employed. The chemical composition of white Portland cement analyzed with X-ray fluorescence (XRF) according to GB/T 19140-2003 is presented in Table 1. The characteristics of EVA and E/VL/VC are shown in Table 2.

2.2. Mix proportions

EV A content and E/VL/VC content in PCBDM were both 10 %, and the pigment content was 3 % (by mass of cement). The sand/cement mass ratio was 4, and the water cement ratio was 0.9.

2.3. Curing and testing methods

2.3.1. Test of efflorescence

The efflorescence samples were prepared as follows: PCBDM was smeared on the surface of cement fiber board (300×210×10 mm) to form a layer with 5 mm thickness according to JC/T 1024-2007. (1) Water drops test

After samples were cured for 5 min, 30 min, 2 h, 4 h, 6 h,
8 h, 10 h, 12 h and 24 h respectively at (23 ± 2)°C/ (50 ± 5) % RH, three water drops were dripped on the surface of samples. Digital camera was used to record the efflorescence after water drops drying.

(2) Water-soaking test

The samples were soaked in water for 8 h after cured at (23 ± 2)°C/(50 ± 5) % RH for 7 d, then digital camera was used to record the efflorescence level after drying.

2.3.2. Test of surface salts leachability

Cylinder PCBDM samples with 90 mm in diameter and 5 mm in thickness were prepared with plastic mold and cured at (23 ± 2)°C/(50 ± 5) % RH for 1 d, 7 d and 28 d, and all samples were covered with plastic sheets until tested. As shown in Fig. 1, the supper surface of samples was exposed to 20 mL deionized water with other surfaces sealed off. After immersion for 4 h, the leaching solution left was collected completely and dried under (70 ± 2)°C. The weight of the residual materials after drying was used to calculate the surface salts leachability as follows:

\[ L_{s,a} = m / (A \cdot t) \]

where \( L_{s,a} \) is the surface salts leachability, g/(m\(^2\)·h); \( m \) is the weight of residual materials in leaching solution after drying; \( g \) is the supper surface area of samples, m\(^2\); \( t \) is the immersion time, h.

2.3.3. Test of soluble salts content in PCBDM

The soluble salts contents in PCBDM cured for 7 d before and after immersion were both tested, and the immersion process was performed as described in 2.3.2. The cylinder sample was divided into 5 layers with 1 mm thickness from the upper to lower surface (as shown in Fig. 1). For each layer, 1 g of grinding mortar was added to 20 mL deionized water in a covered container and stirred with a rotor for 4 h. Then the leaching solution was collected completely and dried under (70 ± 2)°C, leaving only the leached soluble materials, which were then weighed. The soluble salts content in PCBDM was the average value of soluble salts contents of these 5 layers, and the calculation formula is as follows:

\[ L_{s,a} = (m_{a,1} + m_{a,2} + m_{a,3} + m_{a,4} + m_{a,5})/5 \]

where \( L_{s,a} \) is the soluble salts content in PCBDM, mg; \( m_{a,1}, m_{a,2}, m_{a,3}, m_{a,4}, m_{a,5} \) is the soluble salts content of each layer, mg.

2.3.4. Test of inner ions leachability

The samples preparation, curing methods and the acquisition method of leaching solution were the same as described in 2.3.3. The leaching solution was filtered for ions leachability test, and Ca\(^{2+}\), Na\(^+\), and K\(^+\) ions concentrations were tested with Inductively Coupled Plasma Mass Spectrometer (ICPMS 7700) produced by Agilent technologies Inc.

2.3.5. Test of Surface hydrophobility

The samples preparation and curing methods were the same as described in 2.3.1. Water drops were dripped on the surface of samples cured for 28 d, and digital camera was used to record the water drops shape.

2.3.6. Analysis of surface topography

Samples were prepared and cured for 28 d as described in 2.3.1. The surface topography was observed and recorded through light microscopy with maximum magnification of 35×.

3. RESULTS

3.1. Efflorescence

3.1.1. PCBDM cured for less than 1 d

The efflorescence present on the surface of PCBDM cured for 5 min to 24 h is shown in Fig. 2. After PCBDMs were cured for 5 min, 30 min, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h respectively, three water drops were dripped vertically on the surface of each PCBDM from left to right; moreover, the white points revealed that efflorescence occurred, and no white points revealed that no efflorescence occurred. So only slight efflorescence occurs on the surface of reference PCBDM without redispersable powders cured for 5 min; and no efflorescence occurs during longer curing time (Fig. 2, a). EVA-modified PCBDM shows slight efflorescence when cured for 5 min and 30 min (Fig. 2, b). However, E/VL/VC-modified PCBDM exhibits apparent efflorescence until 24 h curing (Fig. 2, c). It can be drawn that when the redispersible powder content is 10 %, EVA slightly prolongs efflorescence duration on the surface of fresh PCBDM; however, E/VL/VC prolongs efflorescence duration more greatly and exacerbates the efflorescence of fresh PCBDM.

3.1.2. PCBDM cured for 7 d

The efflorescence of hardened PCBDM cured for 7 d is shown in Fig. 3. No visual efflorescence is found on the surface of reference PCBDM (Fig. 3, a) and E/VL/VC-modified PCBDM (Fig. 3, c); however, apparent efflorescence occurs on the surface of EVA-modified PCBDM.
Fig. 2. Efflorescence on the surface of PCBDM cured for less than 1 d. Three vertical water drops were dripped on the surface of each board from left to right when cured for: 5 min, 30 min, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h and 24 h. a – reference; b – 10 % EVA-modified; c – 10 % E/VL/VC-modified

Fig. 3. Efflorescence level of PCBDM cured for 7 d tested with water-soaking method: a – reference; b – 10 % EVA-modified; c – 10 % E/VL/VC-modified

(Fig. 3, b). It can be drawn that EVA exacerbates the efflorescence of PCBDM cured for 7 d; while E/VL/VC does not increase the efflorescence of PCBDM, and the actual effect of E/VL/VC on efflorescence needs further research.

3.2. Surface salts leachability

The surface salts leachability was used as a quantitative measure to describe the efflorescence extent of hardened PCBDM, based on the fact that salts mobility is the primary cause of efflorescence. The surface salts leachability of PCBDMs cured for 1 d, 7 d, and 28 d is shown in Fig. 4.

Fig. 4. Surface salts leachability of PCBDMs

Results show that when the curing age is short as 1 d, the surface salts leachability increases by 29 % and 6 % with the addition of EVA and E/VL/VC respectively. When the curing prolongs to 7 d and 28 d, the surface salts leachability increases by 29 % and 55 % respectively with the addition of EVA, while decreases by 39 % and 44 % respectively with the addition of E/VL/VC. Moreover, with the curing prolonging from 1 d to 28 d, the surface salts leachability of reference, EVA-modified and E/VL/VC-modified PCBDM all decrease gradually, and the decrease rates are 75 %, 70 %, and 87 % respectively. It can be concluded that EVA increases the surface salts leachability, and exacerbates the efflorescence of PCBDM. E/VL/VC increases the surface salts leachability of PCBDM cured for 1 d and promotes its efflorescence, which is consistent with the results shown in Fig. 2; otherwise, E/VL/VC decreases the surface salts leachability during longer curing ages, and reduces the efflorescence.

3.3. Inner soluble salts content

The soluble salts content in PCBDM with 5 mm thickness before and after immersion is shown in Fig. 5. Before immersion, the inner soluble salts content of PCBDM increases by 94 % with the addition of EVA; while decreases by 20 % with the addition of E/VL/VC. Compared with that before immersion, the soluble salts content after immersion in EVA-modified PCBDM decreases by 17 %, while in reference and E/VL/VC-modified PCBDM increase by 33 % and 27 % respectively.

3.4. Inner soluble ions content

The soluble Ca\(^{2+}\), K\(^+\), Na\(^+\) ions content in PCBDM cured for 7 d is shown in Fig. 6.

Fig. 5. Soluble salts content in PCBDMs with 5mm thickness cured for 7 d

Before immersion (Fig. 6, a), with the addition of EVA, the Ca\(^{2+}\), K\(^+\), Na\(^+\) ions contents increase by 118 %, 25 %, 68 % respectively; with the addition of E/VL/VC, the Ca\(^{2+}\)
ions content decreases by 24%, the K⁺ ions content almost has no change, while the Na⁺ ions content increases by 58%. It can be drawn that EVA increases the soluble Ca²⁺, K⁺, Na⁺ ions contents in PCBDM; E/VL/VC also increases the Na⁺ ions content, but decreases the soluble Ca²⁺ ions content. After immersion (Fig. 6, b), compared with that before immersion, the Ca²⁺, K⁺, Na⁺ ions contents increase by 56%, 5%, 100% respectively in reference PCBDM, while decrease by 28%, 46%, 12% respectively in EVA-modified PCBDM. In E/VL/VC-modified PCBDM, the Ca²⁺ ions content increases by 180%, while the K⁺, Na⁺ ions contents decrease by 18%, 32% respectively. The total amount of Ca²⁺, K⁺, Na⁺ ions in reference and E/VL/VC-modified PCBDM increases 55% and 121% respectively, but decreases by 27% in EVA-modified PCBDM. It can be concluded that EVA promotes the migration of Ca²⁺, K⁺, Na⁺ ions to the surface. E/VL/VC also promotes the migration of K⁺, Na⁺ ions, but decreases the migration of Ca²⁺ ion; and the total migration of these three ions is decreased.

![Graph of soluble ions concentration in PCBDM cured for 7 d](image)

Fig. 6. Soluble ions concentration in PCBDM cured for 7 d: a – before immersion; b – after immersion

![Photos of PCBDMs exhibiting surface hydrophobicity](image)

Fig. 7. Photos of PCBDMs exhibiting surface hydrophobicity: a – reference; b – 10 % EVA-modified; c – 10 % E/VL/VC-modified

![Microscope images of the surface of PCBDMs](image)

Fig. 8. Microscope images of the surface of PCBDMs: the magnifications of the top and lower images are 7× and 20× respectively: a – reference; b – 10 % EVA-modified; c – 10 % E/VL/VC-modified

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3.5. Surface hydrophobicity

Fig. 7 exhibits the surface hydrophobicity of PCBDMs cured for 7 d. Water drops dripped on the surface of reference PCBDM are absorbed immediately (Fig. 7, a). On the surface of EVA-modified PCBDM (Fig. 7, b), water drops spread slowly and then are absorbed completely after several minutes. The surface of E/VL/VC-modified PCBDM exhibits excellent hydrophobicity (Fig. 7, c), and water drops can remain bead shapes for about 1.5 h.

3.6. Surface morphology

The microscope images of PCBDMs surfaces with magnification of 7× and 20× are shown in Fig. 8.

The image with 7X of reference PCBDM reflects that its surface is rugged, and lots of unblocked pores are observed on the image with 20× (Fig. 8, a). Smooth surface with lots of larger pores is observed on EVA-modified PCBDM (Fig. 8, b); when observed under 20×, it can be found that finner pores are blocked by white efflorescence deposits, while most of larger pores are unblocked; moreover, the diameter of the finer unblocked pores such as P1 was 16 μm and the diameter of the larger unblocked pores such as P2 was 35 μm. Otherwise, few pores are blocked by white efflorescence deposits on the surface of E/VL/VC-modified PCBDM (Fig. 8, c), moreover, most of unblocked pores are non-communicated observed under 20×.

4. DISCUSSIONS

Efflorescence is generated when salts dissolve in the pore water and migrate to the surface where they precipitate; hence soluble salts in mortar and their migration are the keys influencing efflorescence. The content of soluble salts in mortar affected by raw materials reflects the potential risk of efflorescence. However, the effect factors of soluble salts migration are much more complicated. Pores in mortar supply passages for salts migration, and the influence of pore size distribution cannot be ignored. The finner the pores are, the stronger the surface tension of the water in them, and consequently the rate of moisture transfer and salts migration will be faster. However, the finner the pores are, the more easily they are blocked by cement hydrates or efflorescence deposits [13]. The invasion of external water is the migration medium of soluble salts for hardened mortar. Mortars with excellent hydrophobicity can prevent water penetrating, and little water-soluble salts diffuse into or out of mortar. In this paper, the soluble salts content of mortar before immersion was tested as a quantitative measure of the tendency towards efflorescence, and the change of soluble salts content after immersion was tested to evaluate their migration.

4.1. Influence mechanism of EVA on efflorescence

EVA prolongs the setting time [14] and the water-saturated state of mortar, so it prolongs the efflorescence duration on the surface of fresh PCBDM. In hardened PCBDM, EVA increases the content of soluble salts such as Ca$^{2+}$, K$^+$, Na$^+$ ions. There are evidences of chemical interaction of acid groups released by alkaline hydrolysis of EVA with Ca$^{2+}$ ions in the pore water of the cement pastes, and the products of this interaction are calcium acetate and polyvinyl alcohol [10]. The solubility of calcium acetate and calcium hydroxide at 20°C is 34.7 g and 0.6 g respectively, so the soluble Ca$^{2+}$ ions content increases with the conversion of calcium hydroxide to calcium acetate in the presence of EVA. Moreover, EVA increases the larger pores unblocked on the surface of PCBDM. When intruded with external water, EVA increases the inner soluble salts migration amount, and promotes the migration of Ca$^{2+}$, K$^+$, Na$^+$ ions to surface. So EVA increases the salts leachability on the surface of PCBDM, and exacerbates efflorescence occurring.

4.2. Influence mechanism of E/VL/VC on efflorescence

Deionized water was dripped on the surface of E/VL/VC-modified PCBDM cured at (23 ±2) °C/ RH(50 ±5) % for 30 min until water layer forming, and then lots of white powder particles dissolved in the water layer to form suspension liquid as shown in Fig. 9. The suspension liquid was collected and dried in the oven of 40°C. The X-ray diffraction pattern of Portland cement, E/VL/VC and the white powder particles dissolved in the water layer is shown in Fig. 10.

![Graph of suspended substances on the surface of fresh E/VL/VC-modified PCBDM](image)

![XRD pattern of Portland cement (a), E/VL/VC (b) and the white powder particles dissolved (c)](image)

It can be seen that in the white powder particles dissolved (Fig. 10, c), CaCO$_3$, K$_2$Na(SO$_4$)$_2$, (Na,K)$_2$SO$_4$ is the main crystal material. Moreover, these CaCO$_3$ peaks...
in the white powder particles dissolved have good match with that in E/VL/VC (Fig. 10, b), and CaCO₃ is added as anti-caking agent in E/VL/VC. But most peaks only existing in Portland cement (Fig. 10, a) such as C₃S, C₅S, K₂SO₄ are not contained in the suspended substance, which means that the white powder particles dissolved did not contain Portland cement. The white powder particles dissolved were E/VL/VC powder migrating from fresh PCBDM as other polymers such as CE and PVA [15, 16], and E/VL/VC powder suspends on the surface to form efflorescence, so the efflorescence of fresh PCBDM is exacerbated.

In hardened PCBDM, E/VL/VC decreases the soluble salts content, especially for Ca²⁺ ions content, and improves the surface hydrophobicity to prevent water penetrating into mortar; moreover, this mortar has excellent hydrophobicity over 5-year curing [17]. So E/VL/VC prevents water-soluble materials diffusing into or out of the mortar. Moreover, most of pores on the surface of E/VL/VC-modified PCBDM are unconnected, and inner soluble salts cannot migrate through these non communicating pores. So E/VL/VC prohibits the migration of soluble salts to the surface, and reduces the efflorescence of PCBDM.

5. CONCLUSIONS

EVA slightly prolongs the efflorescence duration time on the surface of fresh PCBDM, and exacerbates the efflorescence of hardened PCBDM. In hardened PCBDM, EVA increases the soluble salts content and the larger pores unblocked on the surface, so promotes the migration of inner salts.

E/VL/VC exacerbates the efflorescence of fresh PCBDM due to it easily dissolves in the surface water. However, E/VL/VC reduces the efflorescence of hardened PCBDM, that is because E/VL/VC decreases the soluble salts content, and prohibits the migration of inner salts due to that most of pores unblocked on the surface are not connected and E/VL/VC-modified PCBDM has excellent surface hydrophobicity.

The soluble salts inducing efflorescence of PCBDM specifically refer to Ca²⁺, K⁺, Na⁺ ions, EVA increases Ca²⁺, K⁺, Na⁺ ions contents and promotes their migration, while E/VL/VC decreases Ca²⁺ ions contents, and prohibits the migration of K⁺, Na⁺ ions.

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