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Cement and Concrete Research 33 (2003) 1715–1721

CEMENT AND CONCRETE RESEARCH

Development of polymer films by the coalescence of polymer particles in powdered and aqueous polymer-modified mortars

M.U.K. Afridi [a,*], Y. Ohama [b], K. Demura [b], M.Z. Iqbal [c]

[a] *Dadabhoy Construction Technologies (Pvt) Limited, 5th Floor, Maqbool Commercial Complex,*
Blocks 7 and 8, J.C.H.S. Shahrah-e-Faisal, Karachi, 75350, Pakistan
[b] *Department of Architecture, College of Engineering, Nihon University, Koriyama, Fukushima-ken, 963, Japan*
[c] *Institute of Chemistry, University of the Punjab, Lahore, Pakistan*

Received 15 August 2001; accepted 11 December 2002

Abstract

This paper evaluates and compares the coalescence of polymer particles (continuous polymer films formation) in powdered polymer-modified mortars (PPMMs) and aqueous polymer-modified mortars (APMMs). Polymer-modified mortars (PMMs) using various redispersible polymer powders (powdered cement modifiers) and polymer dispersions (aqueous cement modifiers) were prepared by varying the polymer–cement ratio (P/C) and were tested for the characterization of polymer films using a scanning electron microscope (SEM) after curing for 28 days. It is concluded from the test results that mortar constituents of unmodified mortar (UMM) are loosely joined with each other due to the absence of polymer films, thus having a structure with comparatively lower mechanical and durability characteristics. By contrast, mortar constituents in PPMMs and APMMs are compactly joined with each other due to the presence of interweaving polymer films, thereby forming a monolithic structure with improved mechanical and durability characteristics. However, the results make obvious the poor coalescence of polymer particles or development of inferior quality polymers films in PPMMs as compared to that observed in APMMs. Moreover, PPMMs show less uniform distribution of polymer films as compared to that in APMMs. Different powdered cement modifiers have different film-forming capabilities. However, such difference is hardly recognized in aqueous cement modifiers. The polymer films in PPMMs and APMMs may acquire different structures. They may appear as mesh-like, thread-like, rugged, dense or fibrous with fine or rough surfaces. Development of coherent polymer films is not well pronounced at a P/C of 5% in PPMMs, whereas sometimes coherent polymer films are observed at a P/C of 5% in APMMs. At a P/C of 10% or more, fully developed, coherent polymer films are observed in both PPMMs and APMMs.

Keywords: Polymers; SEM; Mortar; Polymer films

1. Introduction

Polymer-modified mortars (PMMs) using aqueous cement modifiers are widely used as high-performance, low-cost construction materials particularly for finishing and repairing works because of their excellent performance and durability. A later advance for the preparation of PMMs is the invention of powdered cement modifiers with improved qualities having enhanced film-forming characteristics [1]. These powdered cement modifiers are used for the preparation of dry blends to improve handling procedures and to avoid mixing errors [2]. Only water has to be added in the dry blends on the construction site prior to applications [3]. They are often employed to improve the workability and adhesion of fresh cement mortar in Japan, Europe and the USA. In Japan, the powdered cement modifiers are frequently used to produce prepackaged-type products such as decorative wall coatings, tile adhesives and filling compounds for surface preparation [4]. Recently, prepackaged PMMs using powdered cement modifiers have been commercially developed in Pakistan as well.

The importance of continuous polymer films formation in making a monolithic polymer–cement co-matrix in PMMs has already been explained by Ohama [5]. Others [6,7] have also stressed the need of continuous polymer

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* Corresponding author. Tel.: +92-21-455-4749; fax: +92-21-454-8625.

E-mail address: mukafridi@hotmail.com (M.U.K. Afridi).

0008-8846/$ – see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0008-8846(02)01094-3

Table 1
Chemical composition and physical properties of cement

a. Chemical composition

Ignition loss	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Total
1.0	0.1	22.0	5.2	3.2	65.0	1.4	1.8	99.7

b. Physical properties

Specific gravity (20 °C)	Fineness		Setting time		Flexural strength of mortar (MPa)			Compressive strength of mortar (MPa)		
	Residue on sieve of 88 μm (%)	Blaine's specific area (m^2/kg)	Initial set	Final set	3 days	7 days	28 days	3 days	7 days	28 days
3.16	1.4	325	2 h 31 min	3 h 32 min	3.33	4.90	7.16	14.71	24.61	40.88

films for effective polymer-modified cement compositions. The improved properties of PMMs are mainly characterized by such a co-matrix [5].

To understand how polymer phase works in conjunction with the cementitious phase in polymer-modified cement compositions, coalescence of polymer particles was reported mostly by using polymers in dispersion (latex or emulsion) form or employing aqueous cement modifiers [8–14]. However, detailed specific information in this regard is less commonly available mentioning the use of newly developed powdered cement modifiers except for the studies of Semerad et al. [15] where some emphasis has been given to this aspect.

The purpose of this paper is to evaluate and compare the polymer film formation in powdered polymer-modified mortars (PPMMs) and aqueous polymer-modified mortars (APMMs). Such studies will help explain the differences in properties of PPMMs and APMMs, which are sometimes observed, and will also provide basis to further improve the powdered cement modifiers. For this purpose, PMMs using four types of commercially available powdered cement modifiers and two types of commercially available aqueous cement modifiers were prepared with various polymer–cement ratios (P/C) and after processing their samples were observed by a SEM.

2. Materials

2.1. Cement and fine aggregate

Ordinary Portland cement and Toyoura standard sand as specified in Japanese Industrial Standard (JIS) were used in all mixes. The chemical compositions and physical properties of the cement are listed in Table 1a and b.

2.2. Cement modifiers

Commercially available, four powdered and two aqueous cement modifiers were used. The powdered cement modifiers used included one brand of poly(vinyl acetate–vinyl carboxylate) (VA/VeoVa) type and three brands of poly(ethylene–vinyl acetate) (EVA) type. The aqueous cement modifiers used were one brand of EVA emulsion and one brand of styrene–butadiene rubber (SBR) latex type. Their typical properties are given in Table 2. Before mixing, a silicone emulsion type antifoamer containing 30% silicone solids was added to the cement modifiers in a ratio of 0.7% of the silicone solids in the antifoamer to the total solids in the powdered and aqueous cement modifiers.

3. Testing procedures

3.1. Preparation of mortars

PPMMs and APMMs were mixed according to JIS A 1171 (Method of Making Test Sample of Polymer-Modified Mortar in Laboratory) as follows: cement:standard sand = 1:3 (by weight), P/C (calculated on the basis of total solids in powdered and aqueous cement modifiers) of 0%, 5%, 10%, 15% and 20% and their flows were adjusted to be constant at 170 ± 5. The mix proportions of PPMMs and APMMs are given in Table 3.

Table 2
Typical properties of cement modifiers

Type of cement modifier	Stabilizer type	Appearance	Specific gravity (20 °C)	pH (20 °C)	Viscosity (20 °C, cp)	Total solids
Powdered VA/VeoVa emulsion	Anionic	Milky white powder without coarse particles	1.100	–	–	–
Powdered EVA-1 emulsion	Anionic	Milky white powder without coarse particles	1.180	–	–	–
Powdered EVA-2 emulsion	Anionic	Milky white powder without coarse particles	1.120	–	–	–
Powdered EVA-3 emulsion	Anionic	Milky white powder without coarse particles	1.180	–	–	–
EVA emulsion	Anionic	Milky white aqueous dispersion	1.056	5.2	1600	44.4
SBR latex	Anionic	Milky white aqueous dispersion	1.019	8.5	155	45.8

Table 3
Mix proportions of polymer-modified mortars

Type of mortar	Cement:sand (by weight)	Polymer–cement ratio (%)	Water–cement ratio (%)	Flow
Unmodified	1:3	0	77.5	165
Powdered VA/VeoVa-modified	1:3	5	77.2	172
		10	75.5	172
		15	76.2	173
		20	75.0	168
Powdered EVA-1 modified	1:3	5	73.8	170
		10	75.2	173
		15	73.0	170
		20	73.8	172
Powdered EVA-2 modified	1:3	5	76.2	167
		10	76.5	168
		15	76.2	172
		20	76.2	168
Powdered EVA-3 modified	1:3	5	76.2	168
		10	76.5	170
		15	77.5	168
		20	77.5	169
EVA-modified	1:3	5	72.5	170
		10	66.8	167
		15	63.0	167
		20	59.8	168
SBR-modified	1:3	5	74.2	172
		10	70.6	168
		15	62.8	168
		20	57.7	168

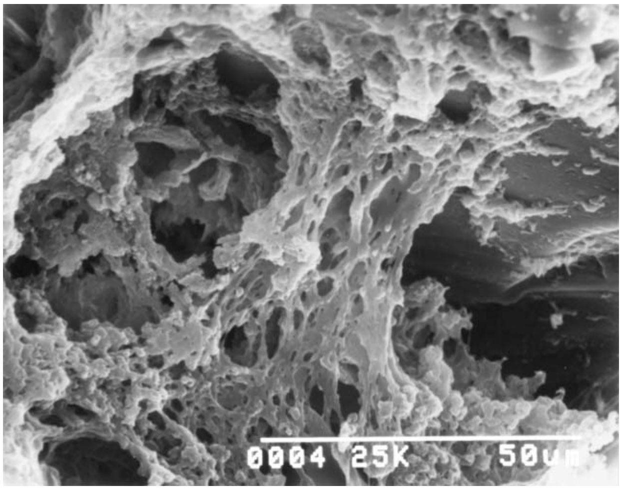

Fig. 2. Powdered VA/VeoVa-modified mortar with a P/C of 20% after 5 h etching with HCl. Fully developed coherent polymer films having mesh-like structure are evident.

3.2. SEM observations

SEM observations for the characterization of polymer films in PPMMs and APMMs were carried out at the age of 28 days using a Hitachi S-510 SEM. To achieve this purpose, mortar specimens 40 × 40 × 160 mm were moulded and cured as follows: 2 days, 20 °C, 80% r.h., moist; 5 days, 20 °C, water; and 21 days, 20 °C, 50% r.h., dry cure. For viewing in SEM, samples 5 × 5 × 7 mm were taken at a depth of 5 mm from the surfaces of the cured specimens and dried in vacuum up to 0.05 Torr by D-dry method for 24 h. After drying, they were fractured by bending in the long direction and attempts were made to remove the inorganic portion of the samples by etching the cross-sections of the samples with 3% hydrochloric acid (HCl) and 55% hydrofluoric acid (HF) for various time intervals up to a maximum of 5 h. After etching, such samples were washed with water and again dried in vacuum up to 0.05 Torr by D-dry method. Before viewing

Fig. 1. UMM after 1 h HCl etching. No polymer film is seen. The mortar constituents are lying apart from each other showing lesser adhesion among themselves due to absence of polymer films.

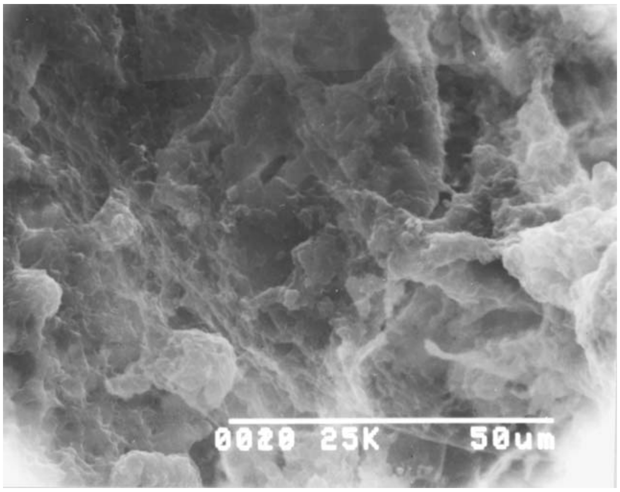

Fig. 3. Powdered EVA-1-modified mortar with a P/C of 15% after 5 h etching with HCl. Fully developed coherent polymer films are evident. Non re-emulsified polymer particle is also seen.

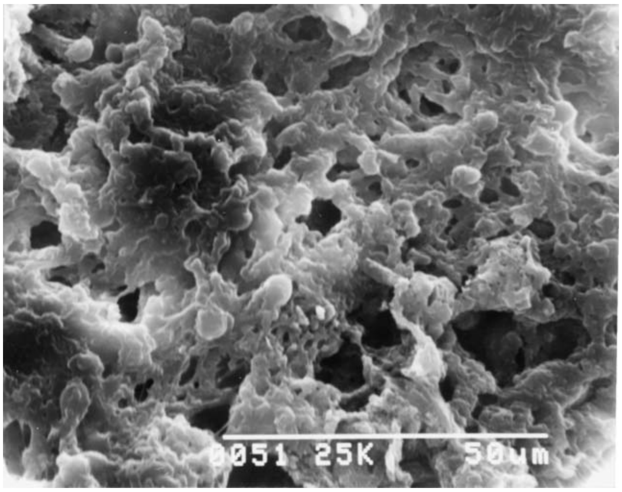

Fig. 4. Powdered EVA-3-modified mortar with a P/C of 20% after 5 h etching with HCl. Fully developed coherent polymer films with mesh-like structure are observed. Exceptionally higher numbers of non-re-emulsified polymer particles are also noted.

in SEM, however, each sample was gold coated for 2–3 min.

4. Results and discussions

The results show that samples from unmodified mortar (UMM) and PPMMs, irrespective of P/C, withstand etching treatment only with HCl for 1 and 5 h, respectively, after which further etching treatment is not possible due to disintegration of samples. Whereas samples from APMMs, irrespective of the P/C, withstand etching treatment both with HCl and HF for 5 and 3 h, respectively. Hence, PPMMs have improved chemical resistance than UMM and inferior chemical resistance in comparison to APMMs. After etching treatment when handling the samples for further processing, the easiness with which the samples were handled varies in the order as follows: UMM < PPMMs < APMMs.

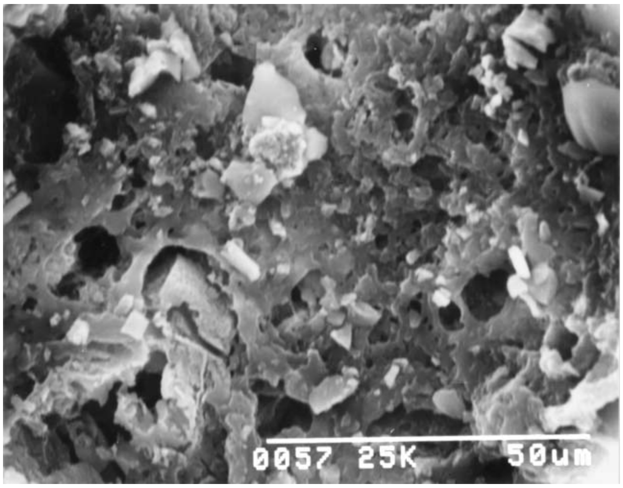

Fig. 5. EVA-modified mortar with the P/C of 5% after 5 h etching with HCl and 3 h etching with HF. Coherent polymer films are evident. Compactness of mortar constituents is also clear.

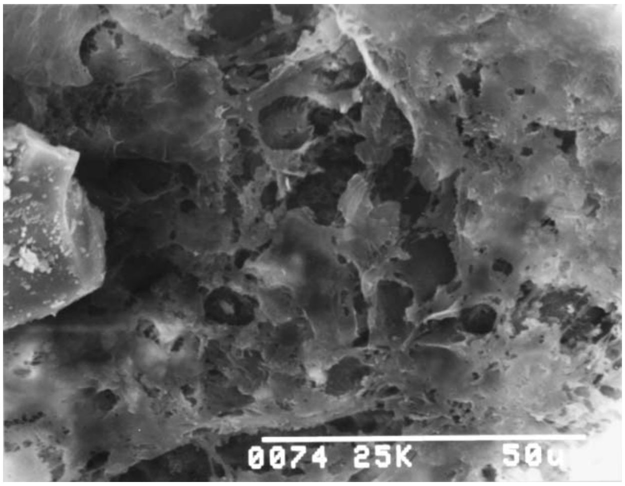

Fig. 6. SBR-modified mortar with a P/C of 15% after 5 h etching with HCl and 3 h etching with HF. Fully developed coherent polymer films having rugged structure are observed.

The reason for the difference in behaviour of the UMM, PPMMs and APMMs is the absence of polymer films in UMM as shown in Fig. 1. This results in the mortar constituents, i.e. cement hydrates and sand grains of UMM, being loosely joined with each other having ultimate lesser adhesion among themselves and lower chemical resistance as compared to those of PPMMs and APMMs. By contrast, the mortar constituents of PPMMs and APMMs are compactly joined, have ultimate improved adhesion among themselves and higher chemical resistance due to the presence of polymer films which reinforce the gel network as shown in Figs. 2–11.

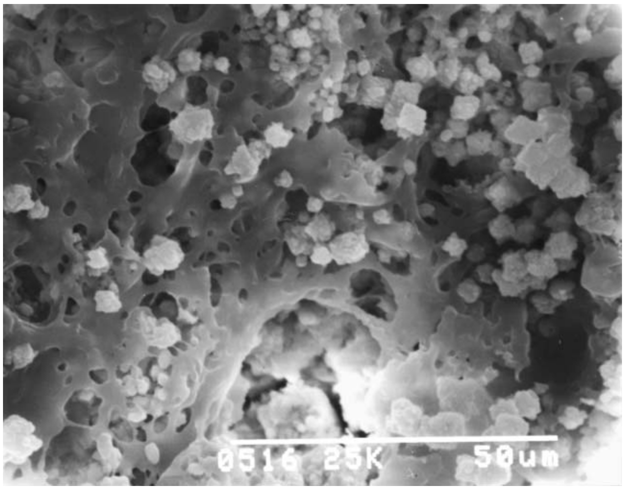

Fig. 7. Portion in SBR-modified mortar with a P/C of 20% after 5 h etching with HCl and 3 h etching with HF. Here, the polymer films appear mesh-like in structure. The cement hydrates still adhering to polymer films showing improved adhesion.

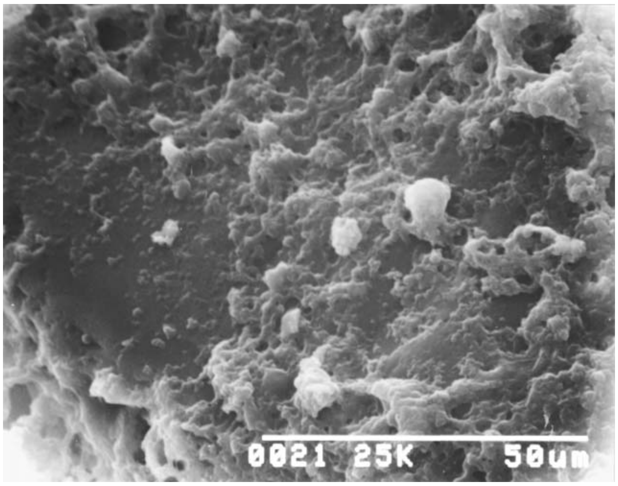

Fig. 8. Another portion of powdered EVA-1-modified mortar with a P/C of 15% after 5 h etching with HCl, showing the absence of polymer films in a particular area. The remaining area of micrograph is covered with poorly developed polymer films and some non-re-emulsified polymer particles.

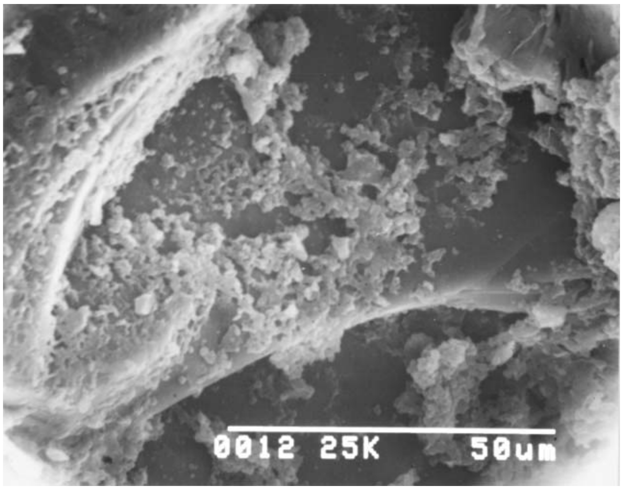

Fig. 10. Powdered VA/VeoVa-modified mortar with a P/C of 5% after 5 h etching with HCl. Less developed polymer films are evident.

Such fully developed, coherent polymer films in PPMMs and APMMs seem to interweave the cement hydrates and sand grains, thus holding the mortar constituents more compactly, simultaneously making elastic interconnections by filling or reinforcing the capillaries and cavities. Hence, polymer films in PPMMs and APMMs provide a supporting action in the system for the transmittance of compressive and tensile strengths like that performed by steel reinforcement with a resultant monolithic structure as also explained by others [8–10]. These effects are clear from Figs. 2–6. However, such polymer films may acquire different structures in PPMMs and APMMs. Sometimes they appear mesh-like as shown Figs. 2, 4 and 7. In Fig. 7, the cement hydrates are still adhering to polymer films, even after acid etching with both HCl and HF showing more improved adhesion between cement hydrates and polymer films in APMMs. While in some cases the structure of polymer films is rugged as shown in Fig. 6.

The differences in the behaviour of PPMMs and APMMs with regard to etching treatment, chemical resistance and handling of samples as mentioned above are related to the fashion in which coalescence of polymer particles occurs in such mortars or to the quality of polymer films developed in them. The results therefore make obvious the poor coalescence of polymer particles or development of inferior quality polymer films having lesser adhesion to mortar constituents and lower chemical resistance in PPMMs as compared to that observed in APMMs. This is attested by the more frequent instances in PPMMs when the same sample exhibits both uniform and nonuniform distribution of polymer films as depicted in Figs. 3 and 8. Whereas, APMMs show frequently more uniform distribution of polymer films as evident from Fig. 6. In addition, non-re-

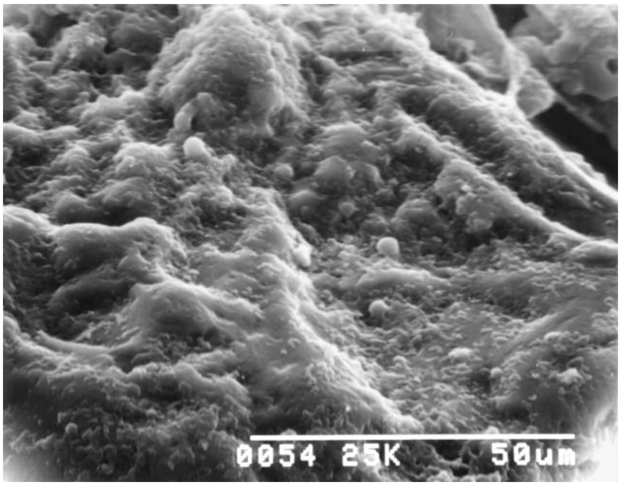

Fig. 9. Locallized area in powdered EVA-3-modified mortar at a P/C of 20% showing non-re-emulsified polymer particles.

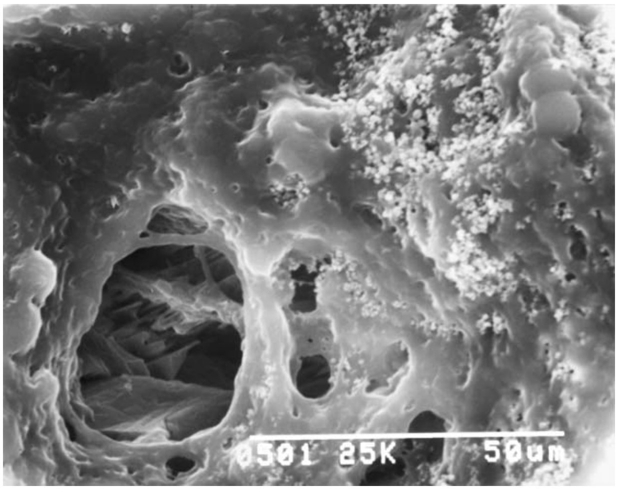

Fig. 11. EVA-modified mortar with a P/C of 10% after 5 h etching with HCl and 3 h etching with HF. Fully developed coherent polymer films having a dense structure and a rough surface are apparent.

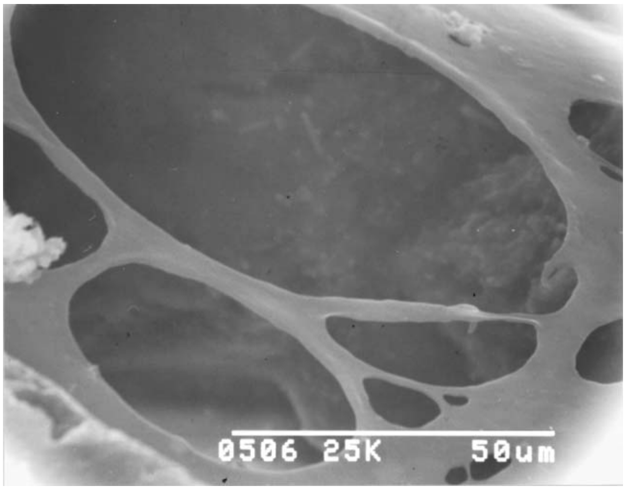

Fig. 12. EVA-modified mortar with a P/C of 20% after 5 h etching with HCl and 3 h etching with HF. Fully developed coherent polymer films having a dense structure and smooth surfaces are evident.

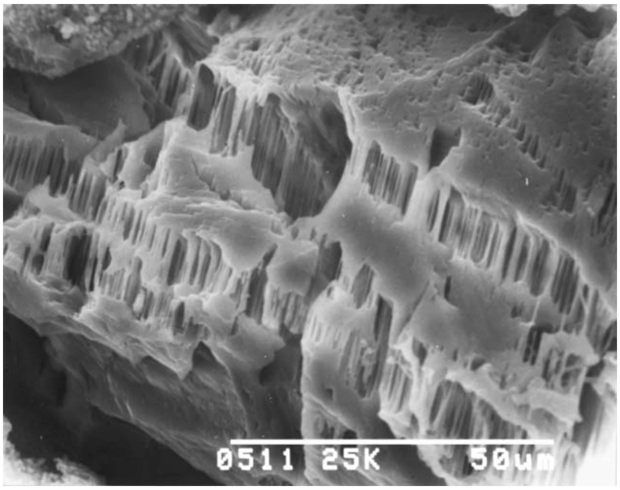

Fig. 14. Another Portion in SBR-modified mortar with a P/C of 20% after 5 h etching with HCl and 3 h etching with HF. Fully developed coherent polymer films having dense structure and fibrous character are seen. Pattern of reinforcement of cavities among mortar constituents by polymer films is also clear.

emulsified polymer particles are also frequently observed along with polymer films in PPMMs as shown in Figs. 3, 4, 8 and 9. Among various PPMMs, powdered EVA-3-modified mortars show the poorest coalescence of polymer particles, as shown in Figs. 4 and 9, compared with the rest of the PPMMs. Hence, different powdered cement modifiers have different film-forming capabilities. Among APMMs, such difference is hardly recognized. Therefore, aqueous cement modifiers have almost the same film-forming characteristics.

Such poor coalescence of polymer particles or development of inferior quality polymer films in PPMMs may be due to the following two possible reasons or because of a combination of these effects as mentioned elsewhere [16]. They include: (i) partial degradation of the properties of surfactants in some portion of the batch during spray-drying process, (ii) because of the nonuniform distribution of solid polymer particles during mixing and improper re-emulsification. As regards the effect of P/C on the development of coherent polymer films is concerned, the development of coherent polymer films is not well pronounced in PPMMs at a P/C of 5% as seen from Fig. 10 for powdered VA/VeoVa-modified mortar, whereas coherent polymer films can be observed at a P/C of 5% in APMMs as shown in Fig. 5 for EVA-modified mortar. However, at a P/C of 10% or more, fully developed coherent polymer films are found in both PPMMs and APMMs as shown in Figs. 2, 3, 4 and 6.

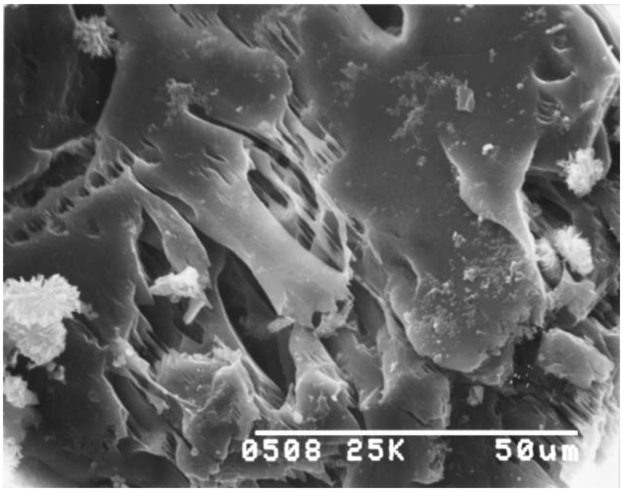

Fig. 13. SBR-modified mortar with a P/C of 10% after 5 h etching with HCl and 3 h etching with HF. Fully developed coherent polymer films having dense structure are observed.

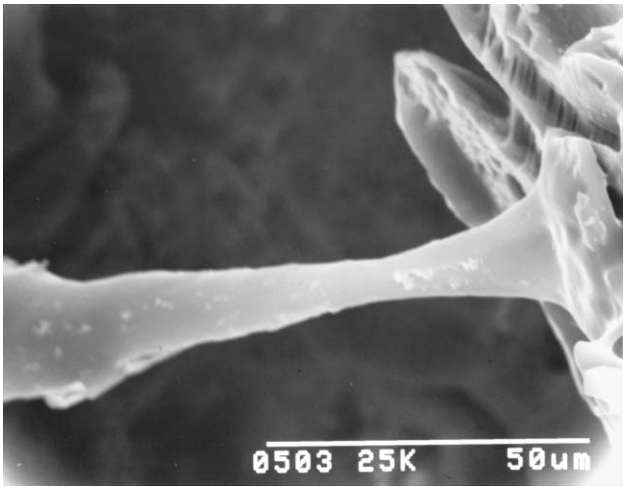

Fig. 15. EVA-modified mortar with a P/C of 20% after 5 h etching with HCl and 3 h etching with HF. Pattern of reinforcement of cavities among mortar constituents by polymer films is clear.

The coherent polymer films having dense structure with rough and smooth surfaces are also observed as shown in Figs. 11 and 12, respectively. The holes in these films represent the spaces originally occupied by sand grains or cement hydrates. Fig. 13 exhibits coherent polymer films having dense structure with some thread-like fibrous character in SBR-modified mortar with a P/C of 10%. With the increase in P/C as depicted in Fig. 14, the structure of polymer films remains dense, however, the thread-like fibrous character becomes more pronounced. Figs. 14 and 15 also make clear the way by which polymer films fill the gap between the cavities of the mortar constituents and intergrow to weave them as mentioned earlier. This eventually helps to improve various mechanical and durability properties of PPMMs and APMMs.

5. Conclusions

(i) Mortar constituents of UMM are loosely joined with each other due to the absence of polymer films, thus having a structure with comparatively lower mechanical and durability characteristics. By contrast, mortar constituents in PPMMs and APMMs are compactly joined with each other due to the presence of interweaving polymer films, thereby forming a monolithic structure with improved mechanical and durability characteristics.
(ii) The results make obvious the poor coalescence of polymer particles or development of inferior quality polymer films in PPMMs as compared to that observed in APMMs.
(iii) PPMMs show less uniform distribution of polymer films as compared to that in APMMs.
(iv) Different powdered cement modifiers have different film-forming capabilities. However, such difference is hardly recognized in aqueous cement modifiers.
(v) The polymer films in PPMMs may acquire different structures. They may appear as mesh-like, thread-like, rugged, dense, fibrous with fine or rough surfaces.
(vi) Development of coherent polymer films is not well pronounced at a P/C of 5% in PPMMs, whereas sometimes coherent polymer films are observed at a P/C of 5% in APMMs.
(vii) At a P/C of 10% or more, fully developed, coherent polymer films are observed in both PPMMs and APMMs.

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