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COMPOSITE MECHANISM OF POLYMER MODIFIED CEMENT

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ABSTRACT

Microstructure and composite mechanism of polymer modified cement (PMC) and mortar have been studied. Microstructure of PMC was observed by cryo-SEM. Dispersed polymer particles were observed in the hardened body. Polymer films were observed on the surface of hardened samples and at the interface of cement or aggregate in PMC. The bending strength of PMC was increased by the action of soft polymer particles in the hardened body. Adhesive strength of PMC was improved by the formation of polymer films. Both the particle dispersion of polymer and the formation of polymer films are useful as the composite mechanism of PMC.

Introduction

PMC mortar(or concrete) mixed with a polymer emulsion exceeds ordinary cement mortar (or concrete) in its adhesive properties and crack resistibility. Owing to these superior properties, it has been used as an adhesive for tile or a finishing material(1,2,3,4). Especially in recent years, it h ; found a new use as a repair material for reinforced concrete structures. Further, PMC mad with a powdered type of polymer is now being used as a spraying material.

Although ıe theory of film formation has been adopted in the past to explain the composite mechanis ı of PMC(5,6), a detailed investigation has not been carried out for PMC with a powderec type of polymers. In this paper we intended to make clear the composite mechani: n of PMC mortar mixed with both a polymer emulsion of ethylene vinyl acetate and also the ɔowdered type of polymers.

Experiments

Materials used for the experiment were normal portland cement with a specific gravity of 3.16 and a Blaine specific surface area of 3290cm ^{2}/g, polymer in emulsion and powdered types

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TABLE 1
Properties of EVA polymers

Type	Particle diameter (μm)	Viscosity*3 (cp/20℃)	pH	Solid density (%)
EVA (Emulsion)	0.8*1	4700	5.0	56.4
EVA (Powder)	1.0*2	—	—	100

*1:Turbidity method *2:Cryo-SEM *3:Brookfild Viscosity(30r.p.m)

with a copolymer of ethylene vinyl acetate as is shown in Table 1, and silica sand. To prevent the sample from segregation as far as possible, the sample used for microstructure observation was a paste with a water:cement ratio of 0.50 and having a polymer-to-cement ratio of 0.10. Mixing of materials was carried out as follows: for the polymer emulsion system, cement was added to the mixing water dispersed with polymer emulsion; for the powdered polymer system, the cement mixed with polymer was added to the water and mixing was carried out with the mixer for 3 minutes. After mixing, the prescribed amount of sample was put into a polystyrene sample bottle.

As for the observation of aggregate surface and the measurement of strength, a mortar sample having a water:cement ratio of 0.50 and cement:sand ratio of 1:2 was used . The polymer-to-cement ratio was from 0.025 to 0.2. Standard JISR5201 procedures were adopted for mixing, moulding and testing. It was cured at a temperature of 20 ℃ and with RH of 80%. The size of test pieces was 40X40X160mm. And the bending strength of mortar was measured using 3-point loading and a 100mm span.

Observation of microstructure was made with the aid of a scanning electron microscope (SEM) with Cryo unit(manufactured by TOPCON). Observation of microstructure immediately after the mixing was carried out as follows: immediately after mixing the sample was put on a sample table(about ϕ 1mm), then dipped into liquid propane to freeze it very rapidly. After the surface of the sample was exposed to liquid nitrogen, the frozen sample was evapolated by Au. Cryo-SEM observation of microstructure after hardening was carried out in the same manner for a fragment obtained from a crushed mortar of the prescribed age.

Observation of interface was carried out to make clear the behavior of the polymer on the surface of the cement particle and aggregate after hardening. For the observation of the particle surface, owing to the difficulty of identifying a cement particle after hardening, we used a model sample having a fly ash-to-cement ratio of 0.3, because fly ash had nearly the same particle diameter as cement and a distinct shape.

To clarify the possibility of improvement of adhesion on the surface of PMC and at the interface between PMC and other materials, observation was carried out on the upper surface and lower interface of the hardened polymer modified cement poured onto a teflon sheet, and infrared absorption spectrum was measured with the aid of a powder reflection method FT-IR(manufactured by BIO RAD).

Results and Discussion

Behavior of powdered polymer in alkali aqueous solution

Fig.1 shows a cryo-SEM photograph of powdered polymer taken in an alkali aqueous solution(saturated solution of calcium hydroxide with pH 12.6). Though the original particle diameter of powdered polymer is about 10 μ m, it is separated in an alkali aqueous solution to particles about 1 μ m in diameter. Therefore, in the case where it is mixed with cement, the polymer particles are uniformly distributed in the same manner as the ordinary emulsion type. Accordingly, the composite mechanism of the powdered type may be investigated in the same way as for the emulsion type.

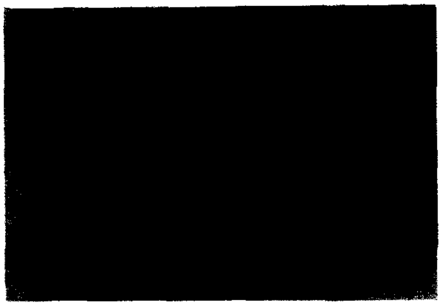


FIG. 1
Cryo-SEM photograph of powdered polymer in alkali solution

Observation of microstructure

Figs.2 and 3, shows the Cryo-SEM photographs immediately after the mixing of PMC including either or polymer emulsion or the powdered polymer. In the case where a powdered polymer was used, it was also observed that spherical particles of the polymer emulsion independently surrounded of cement particles in the same manner as in the case where a polymer emulsion was used.

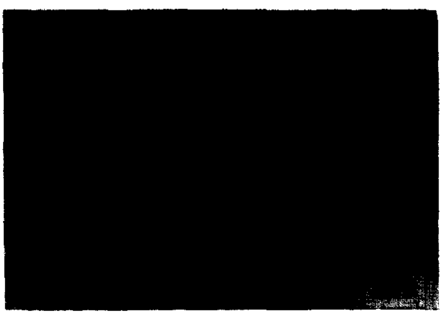


FIG. 2(Emulsion type)

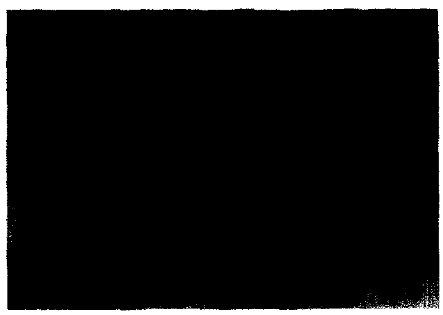


FIG. 3 (Powdered type)

FIGS. 2 and 3
Cryo-SEM photographs of fresh PMC

As for the particle diameter of a polymer particle in a fresh cement paste, in the system on which a polymer emulsion was mixed, it showed a similar value to that measured with a turbidity meter as shown in Table 1. In the system in which a powdered polymer was mixed, it dispersed into as aqueous solution and showed a similar value to that observed by Cryo-SEM. From these results, it is clear that the powdered polymer disperses into cement paste during mixing and behaves in the same manner as the polymer emulsion.

Figs.4 and 5 are Cryo-SEM photographs of the hardened PMC at the age of 3 days mixed with polymer emulsion and a powdered polymer, respectively. The hardened PMC show that the polymer particles which were recognized immediately after mixing were left untouched with cement hydration, it is clear that the polymer particles are dispersed into the hardened cement to form a microstructure, assuming that the cement particles, aggregates, hydrates produced by the hydration of cement and the hardened cement including pores make up a matrix as a whole.

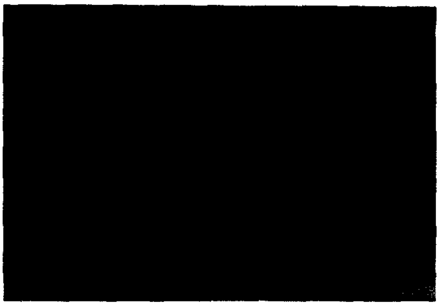


FIG. 4 (Emulsion type)

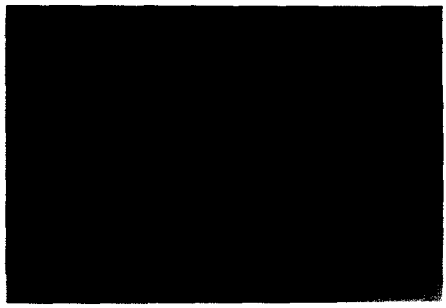


FIG. 5 (Powdered type)

FIGS. 4 and 5
Cryo-SEM photographs of hardened PMC

Fig.6 shows SEM photographs of the hardened mortar mixed with polymer emulsion. As is shown in the photographs, close to the surface of the aggregate there is a layer in which a large number of polymer particles are surrounded by the hydrate. PMC shows a microstructure which consists of uniformly distributed polymer particles surrounded by hydrate. Though the same microstructure is also observed on the surface of aggregates, the amount of polymer calculated from Fig.6 is about 75 vol%, which is about double the amounts of addition.

On the contrary, in the case in which polymer emulsion is not added, no special layer is observed on the surface of aggregate as is shown in Fig.7. Consequently, besides the effect of soft polymer particles distributed in the matrix, the improvement in bending strength of PMC mortar may also be due to the development of an adhesive bond between aggregate and matrix due to the formation of a compound layer consisting of hydrate with abundant polymer particles on the surface of the aggregate.

Figs.8 and 9 show the results of the SEM observation, that is, the comparison between the case where polymer is added to fly ash cement and the case where no polymer is added. In the former case, a dense layer stuck to the fly ash particle is observed.

It is assumed that this phenomenon, which takes place on the surface of a fly ash particle may also be observed on the surface of a cement particle. It is clear that on the surface of a cement particle an interfacial layer exists in which the presence of a polymer suspension may improve the adhesive property of the matrix. It may also be assumed that this also is related to the improvement of bending strength of PMC mortar. However since the fly ash has a pozzolanic reaction while the cement particle has its own hydration reaction, there is a question as to whether the above-mentioned layer is a film made of polymer or a composite made of hydration product and polymer particles; further detailed investigation of this is required.

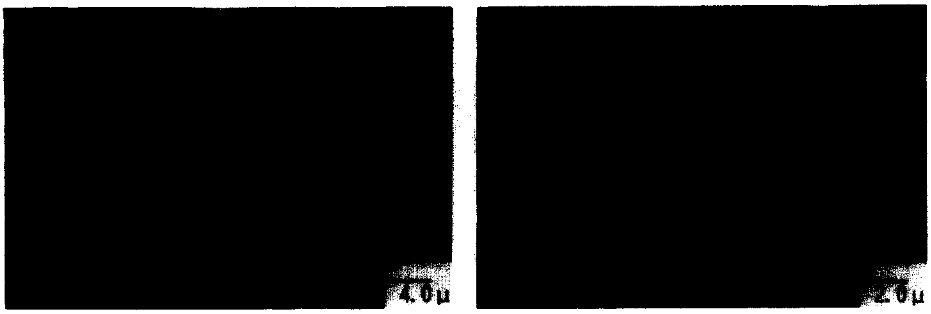


FIG. 6
SEM photographs of hardened PMC mortar

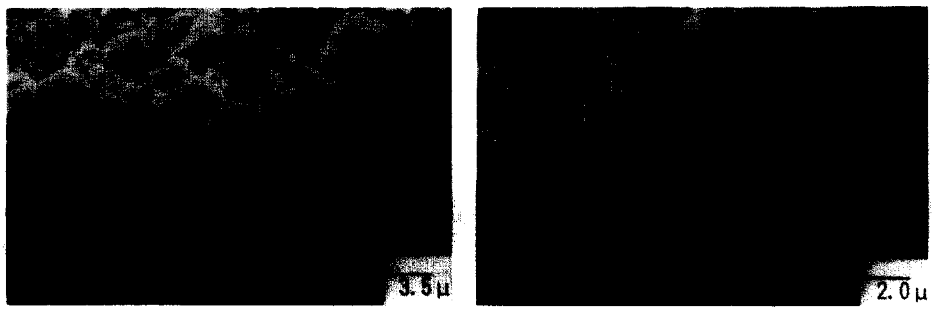


FIG. 7
SEM photographs of hardened ordinary mortar

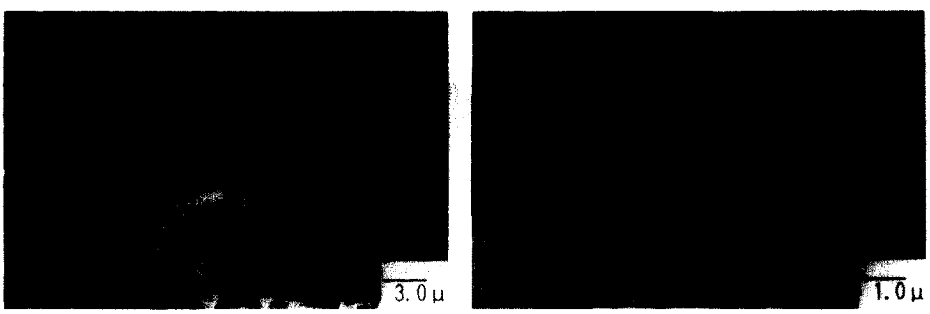


FIG. 8
SEM photographs of hardened PMC paste

Composite mechanism

Fig.10 shows the bending and compressive strengths for each dosage of polymer in PMC with water:cement ratio constant. It shows that compressive strength decrease with an increase of the dosage of polymer. This phenomenon may due to the existence of soft polymer in the hardened cement which has the same effect as pores. On the other hand, bending strength increases with an increase of dosage for low dosages, and then it begins to decrease of higher

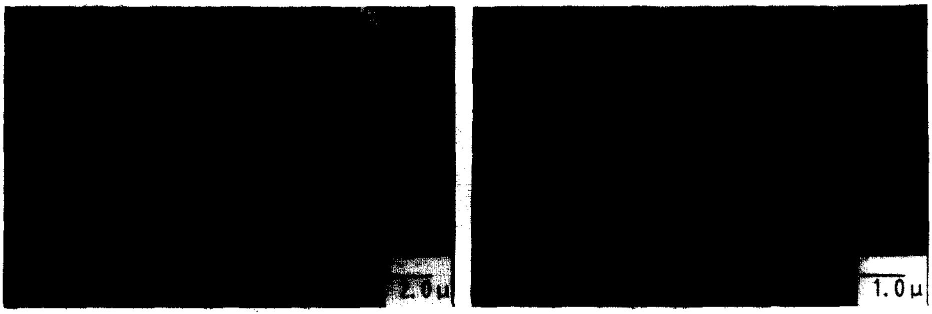


FIG.9
SEM photographs of hardened ordinary cement paste

dosages. This increase of bending strength at low dosages is considered to be due to the effect of the distributed polymer particle. But, owing to the constant water:cement ratio and the behavior of soft polymer particles as pores, the bending strength shows a maximum value at some particular dosage.

For the composite mechanism of the particulate reinforced composite materials, Hasselm and Fulrath (7), Nivas and Fulrath(8) stated that the mean free path(λ) of reinforced particle in a matrix was related to the improvement of strength. The mean free path was caluculated by the following equation(9);

$$\lambda = 4R(1-\phi)/3\phi \cdots\cdots\cdots\cdots [1]$$

where R is the radius of reinforced particle and ϕ is the volume fraction of reinforced particle in matrix. Table 2 shows the calculated mean free path between polymer particles obtained from equation [1] for each dosage of polymer, with mortar, paste and mixing water as the matrix. Since the Cryo-SEM observations showed that the polymer is dispersed in water to separate the hydrate, the calculation based on this assumption is near to the values that of result fromactual observation.

Fig.11 shows the relation between the mean free path of polymer in PMC obtained from equation [1] and the ratio of bending strength-to-compressive strength ratio obtained from Fig.10. The graph shows that the bending strength-to-compressive strength ratio is a remarkably large value in the region where the mean free path of polymer in mortar matrix is about 20 μ m or less. That is, in the region where the mean free path of polymer, the reinforcing particle, is about 20 μ m or less, the crack path in the hardened PMC is complicated, with the result that the bending strength-to-compressive strength ratio becomes large. The dosage of polymer corresponding to the mean free path for which the bending strength-to-compressive strength ratio is improved is about 5% or more, and it coincides well with the already known fact that more than about 5% of polymer dosage is required to improve the bending strength of PMC. In general, to obtain a PMC with the same fluidity, the water:cement ratio can be reduced with the addition of polymer. Therefore, for the dosage for which the ratio of bending strength- to-compressive strength ratio increases, the absolute value of bending strength is also improved.

Adhesive mechanism

Figs.12 and 13 show SEM photographs, displaying the surface of the hardened PMC for the polymer mixed with polymer emulsion poured on the teflon sheet, and the interface between the cement and teflon sheet. In both cases, it is clearly shown that a film is formed. The film may be formed as the result of drying of the polymer particles distributed in the water film on the surface and in the interface. Further, this phenomenon is also observed in the powdered polymer mixed system.

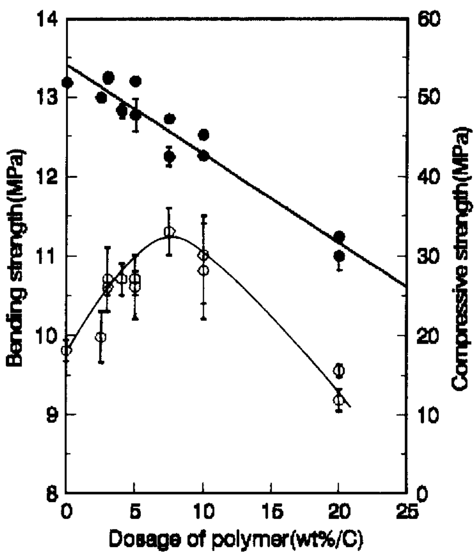


FIG. 10
Bending and compressive strength of PMC

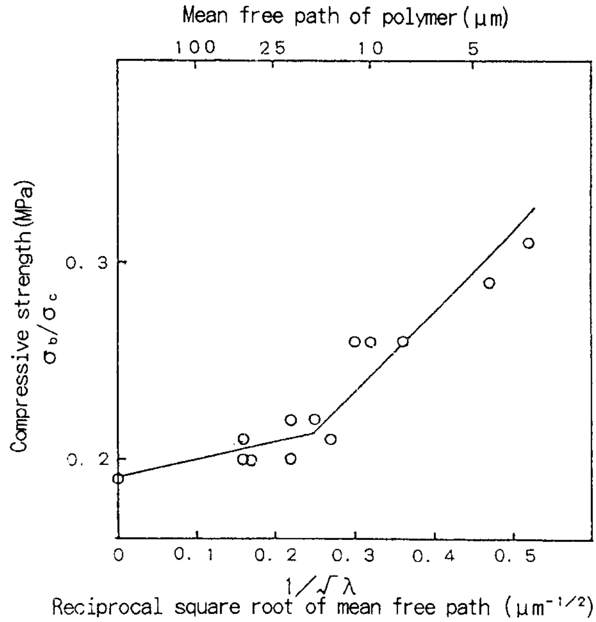


FIG. 11
Relation between the mean free path of polymer and the bending -to-compressive strength ratio

TABLE 2
Calculated mean free path of polymer in hardened PMC

Dosage of polymer (wt%/C)	Mean free path (μm)		
	Mortar matrix	Cement paste matrix	Water matrix
2.5	41.0	21.6	13.2
5.0	20.2	10.8	6.7
7.5	13.5	7.3	4.5
10	9.9	5.4	3.3
20	4.6	2.7	1.6

Fig.14 shows the infrared absorption spectra on the surface of the PMC and in the interface. Both the surface and the interface show such absorption spectra in EVA near 1450cm^{-1}, 2850cm^{-1} and 2950cm^{-1} due to -CH_2- and -CH_3 ,near 1750cm^{-1} due to -COO-, and near 1000cm^{-1} and 1250cm^{-1} due to -CO-. As we have seen, the film formed on the surface of PMC and in the interface were made of polymer. Consequently, the films formed

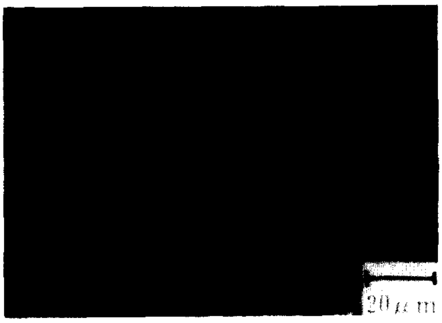


FIG.12 (Surface)

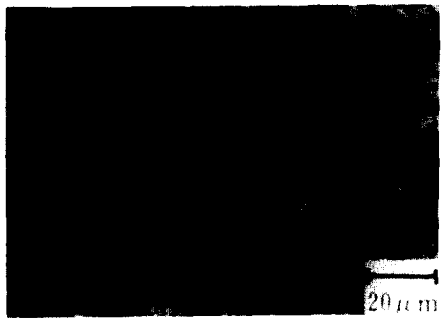
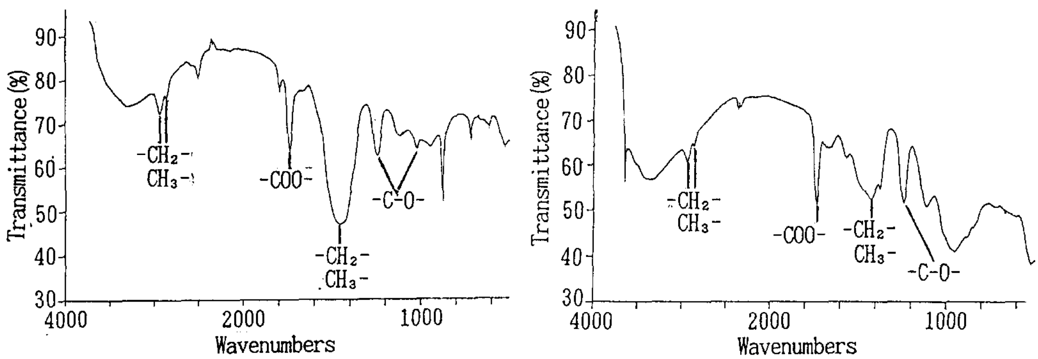


FIG.13 (Intrface)

FIGS. 12 and 13
SEM photographs of surface and interface for hardened PMC

on the surface of PMC and in the interface with the existing concrete, improve the adhesive property of PMC to other materials.



(a)Surface (b) Interface

FIG. 14
Infrared spectra of surface and interface of PMC

Model of the microstructure of PMC mortar and the composite mechanism

A model of the composite mechanism of PMC may be summarized as shown in Fig.15. With cement hydrate as matrix, a microstructure with soft polymer particles distributed in it is formed, and an interfacial layer with different microstructure from the case where no admixture is used form at the surfaces of cement particles and aggregates.

For the aggregate interface, an interfacial layer made of polymer/hydrate composite with a double amount of polymer is generally observed in the matrix of the hydrate. Owing to the crack-scattering effect of soft polymer particles distributed in such a matrix and to the improved adhesive property of the interfacial layer exising in the interface around the cement particle and aggregate, the bending strength and crack resistance of PMC mortar are increased.

Further it is assumed that the adhesive property of PMC mortar can be improved by the development of the bonding property of polymer film formed on the surface of the mortar and in the interface with other materials. Moreover, we are under the impression that the ability of PMC to prevent harmful ions from dispersing is also related to the formation of this film. Further detailed investigation is required on this point.

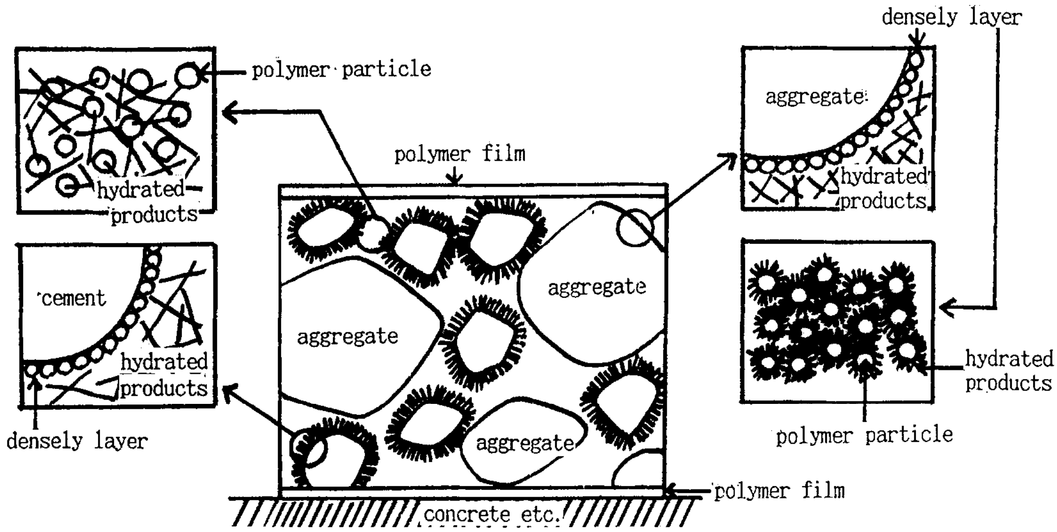


FIG.15
Model of composite mechanism of PMC mortar

Conclusion

We investigated the microstructure and composite mechanism of PMC mixed with either a polymer emulsion or a powdered polymer and made the following observations:
(1) When either a polymer emulsion or a powdered polymer is mixed with cement, spherical polymer particles independently fill the interface between the cement particles, and hydrates produced after hardening crowd around the polymer particles.
(2) When powdered polymer is mixed with either cement paste or alkali solution, it disperses and displays the same behavior as in the case where an ordinary polymer emulsion is used.
(3) The reason for the increase of bending strength of PMC is explained by the action of the polymer particles distributed in the hardened cement as reinforcing particles. The diminishing of the mean free path results in the complication of the propagation course of crack in the hardened cement. For the composite mechanism of PMC it is necessary to consider the particulate reinforced composite type.
(4) The reason why the adhesiveness of PMC to other materials is increased may be explained by the formation of a film in the interface with other materials.

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