ELSEVIER

The Evolution of the Microstructure in Styrene Acrylate Polymer-Modified Cement Pastes at the Early Stage of Cement Hydration

Z. Su,* K. Sujata,† J.M.J.M. Bijen, H.M. Jennings,† and A.L.A. Fraaij*
*Faculty of Civil Engineering, Materials Science Section Delft University of Technology, The Netherlands and †Departments of Civil Engineering, and Materials Science & Engineering, Northwestern University, Evanston, Illinois

The evolution of microstructure in styrene acrylate polymer-modified cement pastes during the early ages of cement hydration has been followed using the environmental scanning electron microscope (ESEM). The investigations show that the polymer influences the microstructure in at least two ways: (1) some of the polymer is adsorbed on cement grains directly after mixing and forms a film that slows the reactions, and (2) the remaining part of polymer is dispersed in the pore water and forms a film after the free water is sufficiently removed by hydration and evaporation. ADVANCED CEMENT BASED MATERIALS 1996, 3, 87–93

KEY WORDS: Hydration products, Microstructure, Polymer dispersion, Portland cement

Polymer dispersions have been used to modify portland cement composites for many years. Polymer cement concrete (PCC) is widely used for overlays on road structures, floors, repairs, and in glass fiber reinforced concrete. The polymer improves a number of properties of concrete: adhesion strength to substrates [1–7], impermeability [8], strain capacity [7,9,10], freeze-thaw deicing salt resistance [7,11,12], and lower curing sensitivity [4]. The process and mechanism by which the microstructure develops, and how it is related to the properties, is still a topic of ongoing research [1,7,9,13,14]. In particular, conventional scanning electron microscope (SEM) has been widely used to characterize the structure of mature (older than 28 days) polymer-modified cement paste [1–3,9,15,16]. Samples must be dried and coated with a thin layer of gold (or carbon) to prevent the surface from charging while being observed. The problem is that drying may cause a distortion of the fragile microstructure [17]. Furthermore, essentially no results have been reported on the influence of polymers on the structure of polymer cement pastes during the early stage of reaction.

This paper presents the results of an investigation into the microstructural development of polymer cement pastes containing a styrene acrylate copolymer dispersion. The results are used to refine a previously proposed model of Su et al. [18].

Background

Several models have been proposed to describe the process of the development of microstructure in polymer-modified cement pastes [1,9]. Some of the common features are as follows: initially, the polymer particles are dispersed uniformly in the liquid phase. Then, as water is consumed by cement hydration, polymer particles gradually agglomerate in the capillary pore system to form a continuous tightly packed layer on the surface of both early products and unhydrated cement grains. Finally, with further removal of water, the packed polymer particles coalesce into continuous films to form a network, which penetrates the hydrate phases and binds them together.

A modification of these general features has been proposed based on analysis of the aqueous phase [14]. The results showed that about 50 to 70% of the particles of a styrene acrylate (SA) dispersion, and even more of a polyvinylidene chloride (PVDC) dispersion, were adsorbed on the surface of cement grains almost immediately after mixing. This means that, for both dispersions, the polymer particles were not uniformly dispersed in the mixing water. At the same time, results showed that as the polymer content increased, the apparent percentage of the adsorbed particles decreased.

Address correspondence to: Hamlin M. Jennings, Department of Civil Engineering, Northwestern University, 2145 Sheridan Road, Room A 133, Evanston, Illinois 60201.

Received May 12, 1994; Accepted May 2, 1995

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/96/$15.00
SSDI 1065-7355(95)00031-L

With an environmental scanning electron microscope (ESEM), it is possible to observe specimens maintained under controlled temperature and pressure (i.e., controlled relative humidity) [17,19–21]. Thus, the specimens experience minimal disruption, particularly at the early stage when the structure is very sensitive to water content.

Materials and Experiments

Materials used in this investigation included: portland cement Type CEM I 32.5 (ENV 197 cement) equivalent to ASTM Type I portland cement (composition shown in Table 1) and a SA dispersion supplied by Forton B.V. in the Netherlands. The SA polymer dispersion had a solid content of 48.6% by mass of the dispersion (at 105°C drying), a pH value of 8.5, and an average particle size of 0.27 μm. The polymer consisted of 50% styrene and 50% butyl acrylate. The dispersion is a nonionic type, containing a deforming agent (Polymeken 1388).

Water:cement ratio (w:c) of the paste was 0.30. This includes the water of the polymer dispersion. The cement pastes contained four volume fractions of polymer (a volume ratio of solid polymer to the sum of the polymer, cement, and water): 0% (control), 8%, 15%, and 25%. Specimens were prepared using the following methods:

1. Cement pastes were prepared by hand-mixing cement with water and polymer dispersion for about 2 minutes outside the microscope. Some samples were observed immediately and others were sealed in a plastic cup until the desired age for observation. The paste, with 25% polymer, was rotated (60 rpm) for 1 day or until used, to prevent settling of coarse cement grains.
2. The specimen with 15% polymer at 3 days was treated with 0.1 N HCl solution for 1 hour to remove the cementitious components.
3. Finally, the companion specimen for Method 2 was heated to 400°C for 3 hours to decompose and vaporize the polymer film.

Samples were observed in the ESEM using a beam voltage of 20 KeV, a beam current of 100 mA, and a working distance of about 8 mm. Fresh pastes (4 hours or younger) were maintained under a pressure of 7.5 torr and a temperature of 9°C, which corresponds to a relative humidity (RH) of 85%. The more mature specimens were observed at the ambient temperature and a pressure of about 5.5 torr in the chamber (RH = 40%).

Results

Observation Directly After Mixing

Immediately after mixing, the structure of the control paste is typically characterized with the formation of $CaSO_4 \cdot 2H_2O$ crystals throughout the paste as shown in Figure 1a. The crystals, likely to be secondary gypsum, have a length of about 5 μm. They form because $CaSO_4 \cdot ½H_2O$ is more solvable than $CaSO_4 \cdot 2H_2O$. And, therefore, the former converts to the latter. The paste with 15% polymer, shown in Figure 1b, has only limited fine $CaSO_4 \cdot 2H_2O$ crystals. This could be due to the fact that the polymer, adsorbed on the surface of $CaSO_4 \cdot ½H_2O$, retarded the conversion of $CaSO_4 \cdot ½H_2O$ to $CaSO_4 \cdot 2H_2O$ crystals. Figure 1b also shows that the edges of cement particles are generally poorly defined. The results may be interpreted as having a structure similar to Figure 1a, except that a film has formed on the surface during the partial drying necessary for observation.

Observation After 4 Hours

After 4 hours of hydration, only calcium silicate hydrate (C-S-H) gel can be seen on the surface of cement grains of the control paste in Figure 2a. The paste modified with 15% polymer is shown in Figure 2b. The surfaces of cement grains are covered by a thin layer of diffuse amorphous polymer phase, with some hydration product. The polymer film can be observed more clearly than directly after mixing, due to the cement hydration and the partial drying as the capillary pore water evaporates in the microscope (RH = 85%).

Observation After 1 Day

After 1 day, C-S-H gel in the control paste completely covers the surface of cement grains and in the "neck regions" between cement grains, and well-developed

TABLE 1. Chemical compositions and properties of portland cement

Chemical Compositions								Specific Surface Area	Specific Density
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O		
63.0%	20.9%	5.5%	3.3%	1.5%	3.4%	0.2%	0.6%	400 m^2/kg	3,100 kg/m^3

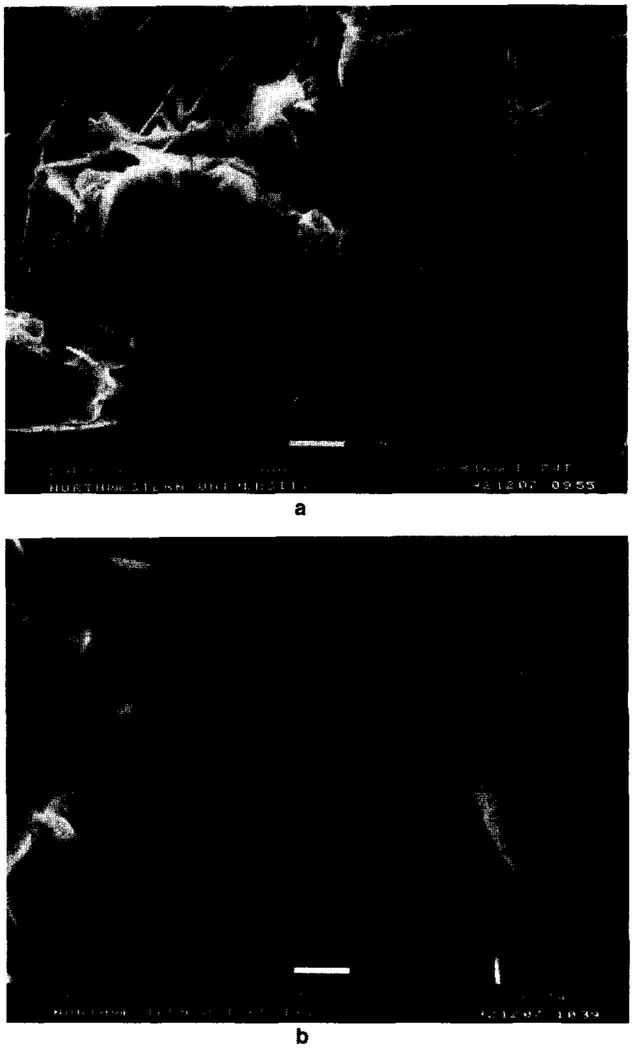

FIGURE 1. The ESEM micrographs showing the microstructure of cement paste immediately after mixing in (a) styrene acrylate 0% (control) and (b) styrene acrylate 15%.

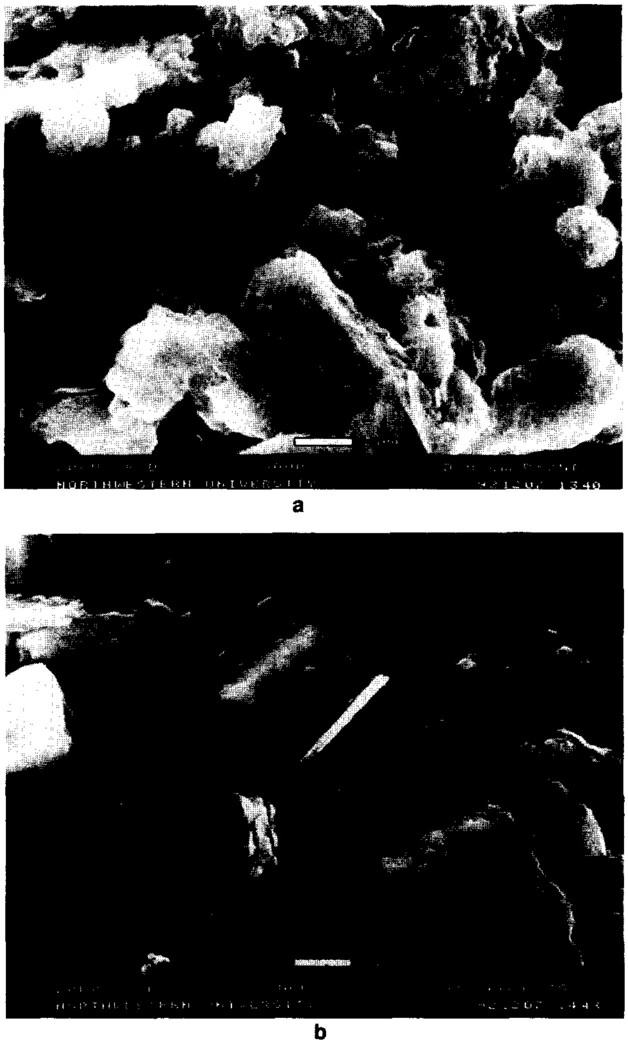

FIGURE 2. The ESEM micrographs showing the microstructure of cement paste 4 hours after mixing in (a) styrene acrylate 0% (control) and (b) styrene acrylate 15%.

crystals of calcium hydroxide have precipitated as shown in Figure 3a. In the polymer-modified pastes as shown in Figure 3b and c, reaction products are now abundant. Figure 3b shows that, in the paste containing 8% polymer, the structure is essentially similar to that of the control. Polymer is not distinguishable, indicating that it is almost completely engulfed by, or incorporated into, the C-S-H gel and other products. The addition of polymer seems to encourage the growth of straight, parallel, sheet- and fiber-like structures as shown in Figure 3c. In contrast to the paste with 25% polymer, no hydration products are observed, and cement particles appear to be covered by the polymer as seen in Figure 3d. Also at 1 day, the polymer film fills the interstices between cement particles and bridges capillary pores.

Observation After 3 Days

At 3 days, the product phases of the control paste and the paste with 8% polymer is denser than it is in younger samples. Typical C-S-H gel structure is present in these pastes, as shown in Figure 4a and b. Figure 4c shows the microstructure of the paste with 15% polymer, in which plate- and needle-shaped hydration products have formed. However, traces of polymer are still visible. The sample containing 25% polymer demonstrates hydration products covered with polymer film throughout the paste, as shown in Figure 4d. However, in all of the polymer modified samples, the plates are long in structure and appear somewhat ordered. In detail, these plates are layered and have smooth surfaces, probably indicating that

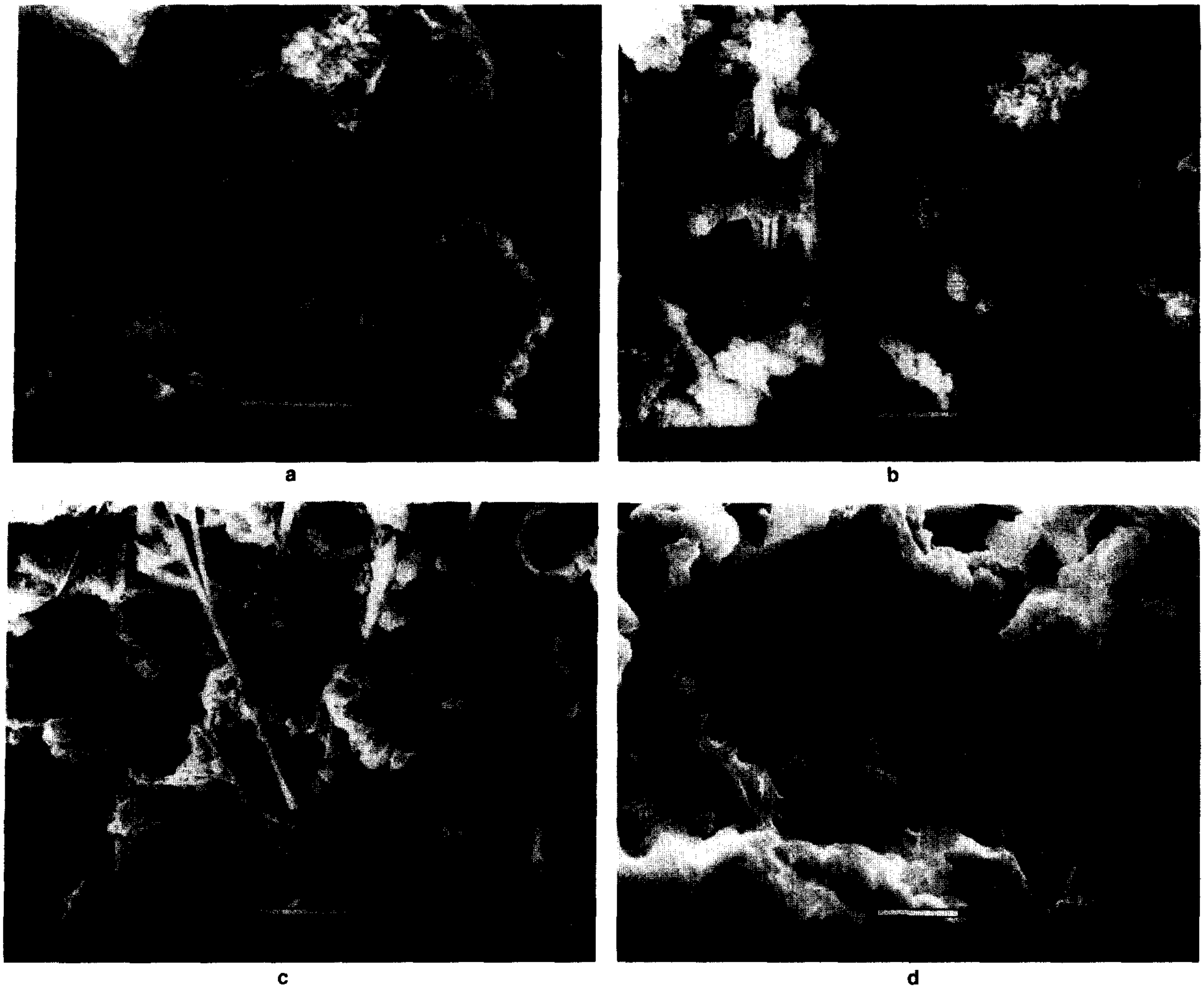

FIGURE 3. The ESEM micrographs showing the microstructure of cement paste 1 day after mixing in (a) styrene acrylate (SA) 0% (control), (b) SA 8%, (c) SA 15%, and (d) SA 25%.

they form from solution, possibly by a coprecipitation process, as opposed to growing from the surface of the unreacted cement particles.

Treated Specimens

Three-day-old specimen, with 15% polymer, was treated with 0.1 N HCl solution for 1 hour. In Figure 5a, a polymer film is seen where cement paste has been etched away. Although some of the needle structure remains, much of the crystalline structure, which may have been supported by the polymer, has disappeared. Thus, the plate-like product contained both inorganic minerals and organic polymer. The specimen that was heated to 400°C for 3 hours shows the polymer film decomposing, leaving behind cement grains with some small granular cement particles and products, as seen in Figure 5b. Also, the crystalline needle-like hydration products have been removed probably indicating an aluminate phase that decomposes at temperatures lower than 400°C.

Discussion

In previous work [14], it was observed that a part of the SA polymer was absorbed on cement grains directly after mixing and another part remained in dispersion. This has been confirmed by the present ESEM results. With increasing polymer contents, a larger percentage of polymer particles becomes dispersed in the mixing water. On the assumption that the polymer is absorbed equally on the cement constituents, and if there are not considerable amounts of hydration products formed after mixing, then the average thickness of a layer of polymer can be calculated. For the cement with a specific surface of 400 m^2/kg, a polymer with an average particle size of 0.27-μm diameter, and a known percentage of the SA polymer adsorbed on cement, the average thickness of the adsorbed polymer layer is shown in Table 2. The thickness of the polymer layer on cement increases with increasing polymer content. The adsorption of a thin layer of polymer film will retard the hydration and setting of cement. This has been confirmed in a previous study [22]. To permit constructive comparisons, some information is included in Table 3. Further details can be found in the work of Su et al. [22].

The role of polymer may be illustrated as follows: The polymer appears to envelop any product that has formed underneath it and the polymer may hamper the access of capillary pore water to the unreacted cement. Thus, the hydration process becomes slower, and setting times become longer compared with the control specimen.

As hydration continues, reaction products push the polymer film outward and eventually penetrate it. This process occurs between 1 and 3 days for the pastes with 8% and 15% polymer as shown in Figure 3b and Figure 4c, respectively. However, for the paste with 25% polymer, the surface of cement grains is still almost covered with polymer film at 3 days.

The higher the concentration of polymer, the more pronounced is the needle- and plate-like morphology. This morphology is apparently composed of polymer and smooth, crystalline hydration products, mainly consisting of calcium, with minor amounts of silicon and oxygen and traces of aluminium, sulphur, and carbon, as confirmed by an electron microprobe analyzer (EMPA). Since these needle- and plate-like structures develop, and because they are neither completely polymer nor hydration product, there must be a synergism between polymer and reaction product during their de-

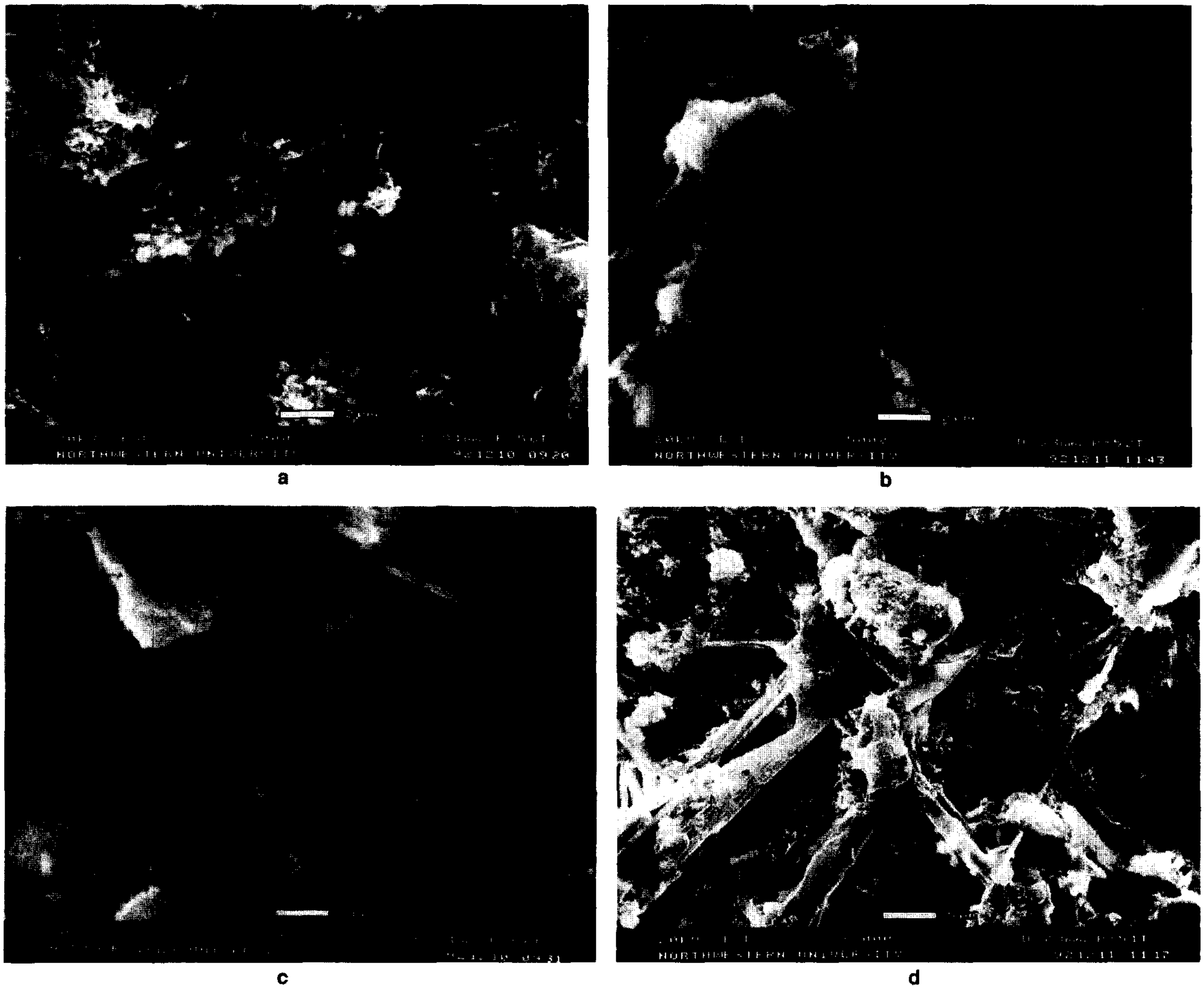

FIGURE 4. The ESEM micrographs showing the microstructure of cement paste 3 days after mixing in (a) styrene acrylate (SA) 0% (control), (b) SA 8%, (c) SA 15%, and (d) SA 25%.

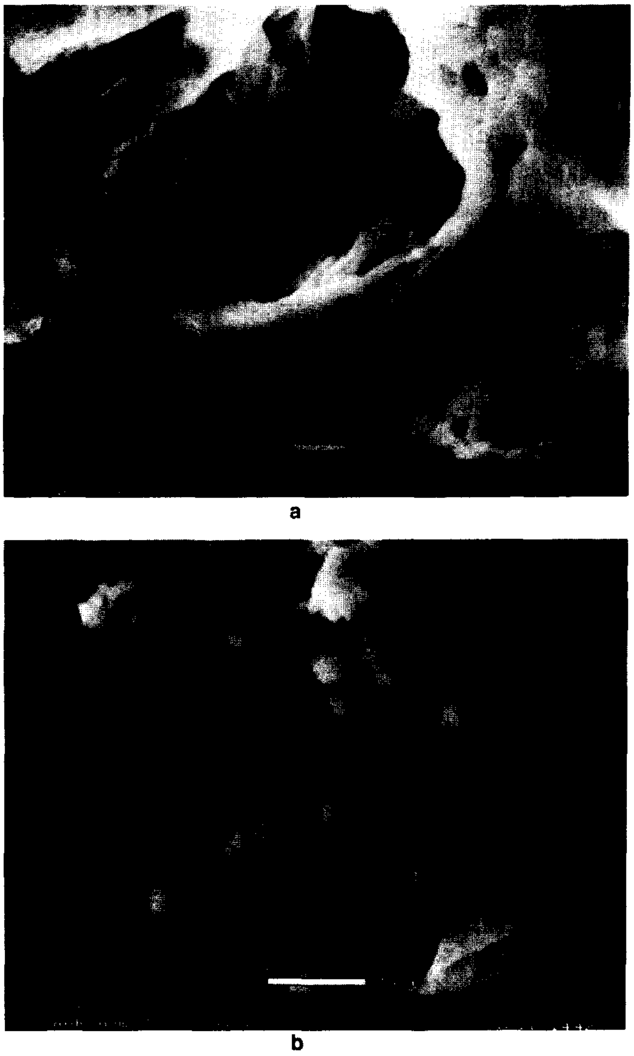

FIGURE 5. The ESEM micrographs showing the microstructure of treated cement paste at the age of 3 days in (a) styrene acrylate 15% (etched) and (b) styrene acrylate 15% (etched and 400°C for 3 hours).

velopment. In other words, neither polymer nor cement alone can produce this morphology. The products must be the result of coprecipitation.

Based on the observation of the hydration process of cement, the model of the microstructure is as follows: *Step 1.* Equilibrium is established between adsorbed and dispersed polymer. The greater the concentration of polymer, the thicker the adsorbed polymer layer. *Step 2.* The polymer layer thickens as water in the capillary pores is consumed. Some products penetrate the polymer layer and other products, probably the crystalline products, precipitate from the pore solution. The dispersed polymer forms necks between cement grains. *Step 3.* The products that form in the pore regions have a distinct plate-like morphology. The morphology depends on the presence of both organic and inorganic phases and may form by coprecipitation. The plates and needles are apparently long in structure and are somewhat ordered.

TABLE 2. The calculated thickness of polymer layer adsorbed on cement grains [14] (based on the Coulter results of cement pastes, 2 hours after mixing)

Polymer Contents in the Paste (%)	Adsorbed Polymer (%)	Thickness of Polymer Film (mm)	Numbers of Polymer Layers
8	69.3*	0.14	0.53
15	62.2	0.26	0.97
25	50.4	0.40	1.48

*Based on the filtration test results in the literature [14].

TABLE 3. Selected information about rate of reaction for polymer-modified cement pastes [22]

Polymer Content (%)	Initial Setting Time (hours)	Final Setting Time (hours)	Age (days)	Hydration Degree (%)
0	2.5	3.2	1	36
			7	56
15	6.0	7.7	1	25
			7	45
25	—	—	1	20
			7	42

Conclusion

Based on the ESEM observations, the following conclusion can be drawn: The results of the ESEM observations of polymer-modified cement pastes show that polymer influences cement reaction in at least two ways: (1) some of the polymer forms a film that slows the hydration reaction and confines the products that form close to, or on, the surface of the cement; and (2) some of the polymer remains dispersed and influences the morphology of products that form from solutions in the capillary pore space. The surface layer forms directly after mixing, and, as water is consumed, it thickens. The product that forms in the pore regions after 3 days is plate- or needle-like. These products are partly inorganic and partly polymer.

References

1. Ohama, Y. *ACI Mater. J.* **1987,** Nov.–Dec. 511–518.
2. Su, Z.; Bijen, J.M.J.M. *Proc. 6th ICPIC* **1992,** 474–481.
3. Pareek, S.N.; Ohama, Y.; Demura, K. *Proc. 6th ICPIC,* **1990,** 442–449.
4. Su, Z.; Bijen, J.M.J.M.; Larbi, J.A. *Cem. Concr. Res.* **1991,** *21,* 726–736.

5. Su, Z. *Ausschuss für Stahlbeton—29. Forschungskolloquium Proceedings*. **1994,** 195–202.
6. Bright, R.P.; Mraz, T.J.; Vassallo, J.C. In *Polymer-Modified Hydraulic-Cement Mixtures,* STP 1176 ASTM (PCN) 04-011760-07; 1993; pp 44–62.
7. Su, Z. Ph.D. Dissertation; Delft University of Technology: Delft, The Netherlands, 1995.
8. Hamimoto, H.; Wakasugi, M. In *Polymer-Modified Hydraulic-Cement Mixtures,* STP 1176 ASTM (PCN) 04-011760-07; 1993; pp 34–43.
9. Grookurth, K.P. *1989 MRS Symp. Proc.* **1989,** *179,* 273–281.
10. Su, Z.; Bijen, J.M.J.M.; Fraaij, A.L.A. *Effects of Dry/Hot-Wet/Col Cycling Tests on the Pore Structure and Properties of Polymer Cement Mortas;* University of Technology: Delft, The Netherlands, 1994.
11. Su, Z.; Bijen, J.M.J.M.; Fraaij, A.L.A. *Effects of Freeze-Thaw Loading on the Pore Structure of Polymer Cement Paste and Concrete;* Delft University of Technology: Delft, The Netherlands, 1994.
12. Bordeleau, D.; Pigon, M.; Banthia, N. *ACI Mater. J.* **1992,** *89,* 547–553.
13. Lavelle, J.A. *ACI Mater. J.* **1988,** Jan.-Feb., 41–47.
14. Su, Z.; Bijen, J.M.J.M.; Fraaij, A.L.A. *1992 MRS Symp. Proc.* **1992,** *289,* 199–204.
15. Bentur, A.; Diab, H.; Ben-Dor, L.; Heitner-Wirguin, C. *Adv. Cem. Res.* **1990,** *3,* 1–7.
16. Fye, B.A. *6th ICPIC* **1990,** 210–217.
17. Lange, D.A.; Sujata, K.; Jennings, H.M. *Ultramicroscopy* **1991,** *37,* 234–238.
18. Su, Z.; Bijen, J.M.J.M.; Fraaij, A.L.A. *A SEM Study of Polymer-Modified Cement Paste and Its Interface with Limestone;* Delft University of Technology: Delft, The Netherlands, 1992.
19. Sujata, K.; Jennings, H.M. MRS Bulletin **1991,** Mar., 41–45.
20. Sujata, K.; Jennings, H.M. *J. Am. Ceram. Soc.* **1992,** *75,* 1669–1673.
21. Sarkar, S.L.; Aimin, X. *Cem. Concr. Res.* **1992,** *22,* 605–608.
22. Su, Z.; Bijen, J.M.J.M.; Larbi, J.A. *Cem. Concr. Res.* **1991,** *21,* 535–544.